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Tunnelling Dilatometry in Low Dimensional Compounds

by

Ian Daniel Maclean

Submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy

at
Dalhousie University, Halifax, Nova Scotia

July, 1992

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Abstract

A new instrument for the measurement of the expansion properties of mechanically weak materials is developed. This device uses a three-terminal capacitance technique in tandem with a negative feedback scheme to monitor length changes in compounds of low quasi-dimensionality with a resolution of 0.1 ppm. A novel technique of "self-heated" expansion allows the calculation of the absolute thermal expansion coefficient without the complication of cell-correction effects. High-resolution thermal expansion results are shown for the quasi-two-dimensional charge-density-wave (CDW) compound 2H-TaSe$_2$. The previously unknown thermal expansion properties of the quasi-one-dimensional CDW compounds o-TaS$_3$ and NbSe$_3$ are presented as well. Measurements of the length changes of the latter two materials as a function of applied electric field allow the estimation of the zero-frequency Young's modulus changes in the non-linear regime. These results are interpreted within a phase-relaxation model of CDW elasticity incorporating a continuous distribution of relaxation times. Refinements of both the instrument and the technique are discussed.
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<tr>
<td>a</td>
<td>Dimerization parameter</td>
</tr>
<tr>
<td>(a_0)</td>
<td>Saturation value of dimerization parameter</td>
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<tr>
<td>AB</td>
<td>Approach barrel</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>b</td>
<td>Capacitor plate lever arm</td>
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<tr>
<td>B</td>
<td>Cubical coefficient of thermal expansion, Sample barrel</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>(C_p)</td>
<td>Specific heat at constant pressure</td>
</tr>
<tr>
<td>(C_v)</td>
<td>Specific heat at constant volume</td>
</tr>
<tr>
<td>(C^{\text{ld}})</td>
<td>Component of stiffness tensor</td>
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<tr>
<td>C/I</td>
<td>Commensurate/Incommensurate</td>
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<tr>
<td>CA</td>
<td>Cantilever</td>
</tr>
<tr>
<td>CCDW</td>
<td>Commensurate charge density wave</td>
</tr>
<tr>
<td>CDW</td>
<td>Charge density wave</td>
</tr>
<tr>
<td>CL</td>
<td>Lower capacitor plate</td>
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<tr>
<td>CO</td>
<td>Cut out</td>
</tr>
<tr>
<td>CT</td>
<td>Cantilever tongue</td>
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<tr>
<td>CU</td>
<td>Upper capacitor plate</td>
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d Distance between capacitor plates
DAC Digital to analog converter
DC Direct current
DVM Digital volt meter

e Emissivity
e_s Coefficient of linear term in the anharmonic potential
e_{rs} Strain tensor
e_o Permittivity of free space
E Young's modulus

f Generalized functional form for the temperature dependence of the free energy
f_o Fundamental CDW noise frequency
\xi_s Coefficient of the square term in the anharmonic potential
F Frame
FB Floating barrel

g Acceleration of gravity, Temperature jump distance
g_s Coefficient of cubic term in the anharmonic potential
G Graphite, Free energy
GA Gallows
Gr  Grashof number
GR  Guard ring

$h_s$  Coefficient of quartic term in the anharmonic potential
HOPG  Highly oriented pyrolytic graphite
HS  Helical spring
HVT  Halogen vapour transport

I  Current
ICDW  Incommensurate charge density wave
I-V  Current-voltage

$k$  Thermal conductivity

$k_F$  Fermi wavevector

$k_o$  Constant term of He thermal conductivity

$k_l$  Term linear in temperature for He thermal conductivity
KR  Knurled ring

$L$  Length (sometimes half-length) of a sample

$L_o$  Rest length of springs in anharmonic model
LB  Lower barrel
M  Transition metal atom
MA  "Milled away"

Nu  Nusselt number
N/ICDW  Normal to Incommensurate charge density wave phase transition
NBN  Narrow band noise

p  Exponent for mechanical frequency dependence of threshold field softening
P  Power consumed by sample
P_c  Critical power (power at the critical temperature)
P_r  Radiated power
Pr  Prandtl number
PA  Peizoelectric actuator
PCT  Power conversion to temperature
PLD  Periodic lattice distortion
PLL  Phase locked loop

q_{CDW}  Charge density wave wavevector

r  Capacitor plate radius, effective dimensionality
r_s  Sample radius
r_w  Radial distance to cavity wall
R  Resistance
Ra  Rayleigh number
RA  Rough approach
RCT  Resistance conversion to temperature

s  Tip to surface distance
\( s_n \)  Elastic compliance tensor
S  Sample
SB  Sample barrel
SP  Leaf Springs
STM  Scanning tunneling microscope

\( t \)  Characteristic time
\( t_F \)  Characteristic relaxation time for a "fixed" CDW
\( t_s \)  Characteristic relaxation time for a "sliding" CDW
\( T_c \)  Transition temperature
\( T_s \)  Temperature of sample
\( T_w \)  Temperature of wall
TD  Tunnelling dilatometer
TF  Tripod frame
TMD  Transition metal dichalcogenide
TMT  Transition metal trichalcogenide
TS Threaded screw

$U_s$ Anharmonic potential

UHV Ultra high vacuum

V Voltage, Volume

$V_G$ V-groove

$w$ Frequency of mechanical vibrations

$x$ Position of CDW with respect to laboratory frame, Chalcogen atom

$X$ Some thermodynamic property

$X^{1\text{H}}$ Thermodynamic property above phase transition

$X^{1\text{L}}$ Thermodynamic property below phase transition

$Y$ Young's modulus or longitudinal elastic modulus

$\alpha$ Coefficient of thermal expansion

$\alpha_{ij}$ Thermal expansion tensor

$\gamma^0$ Anisotropic Gruneisen tensor
$\gamma_{SB}$  Stefan-Boltzmann constant

$\eta_i$  Stress tensor (reduced notation)

$\xi$  Order parameter

$\nu$  Kinematic viscosity

$\theta$  Mean thermal energy per lattice mode

$\Lambda$  Coefficient of square term in anharmonic potential

$\Lambda$  Coefficient of cubic term in anharmonic potential

$\rho$  Charge density, Mass density

$\rho_0$  Unmodulated charge density

$\epsilon$  Strain in basal plane

$\epsilon$  Strain perpendicular to the basal plane

$\phi$  Charge density wave phase
Acknowledgements

The author wishes to express his sincere gratitude for the patient guidance and support of his supervisor, Professor Manfred H. Jericho. He would also like to thank Professor Anthony M. Simpson for the use of his equipment and for his valuable advice. Finally, he must thank the students, faculty and staff of the Department of Physics for the many kindnesses shown him over these years. The author is pleased to acknowledge the financial support of the Faculty of Graduate Studies at Dalhousie University and that of the Sumner Foundation.
Chapter One  Introduction

The aim of this work is two-fold. In the first place the design and operation of a novel instrument for dilation measurement is outlined. In contrast with most of the standard dilatometric techniques (save X-ray diffraction) this apparatus allows the controlled application of uniaxial stress on the samples. This is of particular importance to the measurement of samples which are considered to be "mechanically weak". In the second place the application of this instrument to Charge-Density-Wave (CDW) compounds of low effective dimensionality is reported. In the case of a layered compound, 2H-TaSe$_2$, the sensitivity of the thermal expansion measurement is improved over previous work and an experimental contradiction resolved. In the case of the quasi-one-dimensional compounds, NbSe$_3$ and ω-TaS$_3$, the coefficient of thermal expansion is obtained for the first time. In addition, the structural and elastic properties of these latter compounds are examined as a function of electric fields in excess of threshold.

The expression "mechanically weak" is rather vague outside an experimental context. All the standard dilatometric techniques (with the exception of X-ray diffraction) depend on the sample to mechanically communicate its dilation to some reference object which is constrained to move uni-directionally. This reference object might be an optical flat [1.1], a transformer winding [1.2] or a
capacitor plate [1.3]. In any case, the requirements of stability demand that the sample both support and move the reference object. (The technique of X-ray diffraction is a notable exception to these methods of dilation measurement. However, while X-Ray diffraction makes no mechanical demands on the sample it suffers from two distinct drawbacks. In the first place the sensitivity to dilation is limited by the resolution to which the unit cell can be measured. The technique cannot take advantage of the multiplicative effect of a macroscopic sample and this renders its sensitivity orders of magnitude lower than that of those mentioned above. The second difficulty is that X-ray diffraction has a relatively poor resolution in externally applied fields. The measurement of the unit cell requires a "snapshot" of the sample which demands a minimum counting time. The resolution thus depends on the stability of the external field. If that field is temperature then the situation worsens if only because the X-ray deposits energy in the sample. And of course, this discussion pre-supposes that there is a unit cell to be measured)

There is a group of solids for which these mechanical demands are unreasonable. These materials either are prepared or occur naturally with a high degree of physical anisotropy. For example, such prepared materials might include thin films of organic or inorganic origin, thin fibres spun from polymers or spin-quenched ribbons of various compositions. The naturally occurring examples could encompass the layered structures of mica, graphite or the transition-metal dichalcogenides together with the whisker compounds of the TMT's.
Dilational techniques which make compressive mechanical demands on the load-bearing edges of these materials will certainly fail. Such materials are deemed "mechanically weak". For this entire category little or nothing is known of their dilational properties either as a function of temperature or as a function of electric or magnetic fields.

It would be a simple matter to argue from generalizations that the study of the dilatometric properties of physically anisotropic materials is crucial to both their fundamental description and application. Indeed, for their thermomechanical properties alone such arguments have already been made [1.4]. In this work the motivation is more specific and in its own way has shaped the progress and design of experiments. For this reason attention is drawn to the compounds of low effective dimensionality that undergo a Peierls metal-insulator transition to a CDW state.

The Peierls transition is a soft-mode, metal-insulator transition that has been reviewed extensively in both experimental [1.5] and theoretical literature [1.6]. Certain highly anisotropic crystalline compounds are susceptible to this transition by reason of the high degree of anisotropy present in their Fermi surface topology. It is not enough that materials be prepared in an anisotropic form. Fundamentally, they must exhibit anisotropic electronic dispersion relations.

It is usual to explain the Peierls state through the dimerization of a linear chain metal with a half-filled conduction band [1.6]. This model neglects the effect of fluctuations which are expected to be very strong in such one-dimensional systems.
However, in real materials which are only "effectively" one-dimensional correlations between adjacent chains can mitigate the role of fluctuations. Thus, in a limited sense the linear chain metal (with its three dimensional character understood) provides a reasonable illustration of the effects that result in a Peierls transition.

The linear chain metal in figure 1.1(a) is purely one-dimensional with the lattice constant "a" and has no electron-phonon interaction. The conduction band is half-filled for this exercise but band-filling is unimportant to the general notions that drive this transition. The Fermi surface actually consists of two points at $+k_F$ and $-k_F$. The Brillouin zone is found at the points $+ \pi/a$ and $- \pi/a$. At $T=0$ with a non-zero electron-phonon interaction this chain is always unstable against a macroscopic condensation of $2k_F$ phonons. This condensation implies the formation of a periodic lattice distortion (PLD) which for this half-filled band dimerizes the chain as shown in figure 1.1(b). The phonon condensation creates a new periodicity in the lattice which moves the Brillouin zone inwards to exactly $+k_F$ and $-k_F$. An energy gap must open up at the zone boundary and the size of this gap is proportional to the amplitude of the PLD, "u". All electronic states are lowered by an amount proportional to $u^2 \ln u$ as the metal is transformed to an insulator. This lowering of the electronic energy comes at the cost of an increase in the lattice elastic energy proportional to $u^2$. The chain metal is thus always unstable against this phonon condensation at $T = 0$.

The modification of the electronic dispersion relation results in a periodic
Figure 1.1 (a) Linear chain metal without electron-phonon interaction (b) same chain with electron-phonon interaction (after reference 1.5)
variation in the conduction electron density,
\[ \rho = \rho_o + \rho_1 \cos(2k_Fx + \phi) \] (1)

where \( x \) is the position along the chain direction. This variation is termed the Charge-Density-Wave although the distortion is static.

The effect of finite temperature is to excite electrons across the gap in the single-particle energy spectrum [1.7]. Liberated from the frozen CDW distortion these are free to move and begin to screen the electron-phonon interaction. The increased screening reduces the PLD and consequently the energy gap. As the temperature rises the gap goes to zero in a continuous manner and here there is a second order phase transition back to the undistorted metallic state.

The higher the degree of anisotropy in a real Fermi surface the greater the prospect of a single phonon condensation gapping a large portion of that Fermi surface. Consequently, materials that possess this characteristic tend to be energetically disposed to the Peierls state.

There are many compounds that enter the Peierls state but those that are of interest here are members of the transition-metal trichalcogenide (TMT) group and transition-metal dichalcogenide (TMD) group.

The TMT compounds with chemical formula MX\(_3\) (M-transition metal, X-chalcogen) all share the same basic structural unit: a trigonal prism of chalcogens at the centre of which (or nearly so) lies a transition metal atom. These trigonal prisms are stacked triangular-end to triangular-end to form infinite chains. In bulk form crystals of the TMT class form either ultra-fine whiskers or ribbons.
depending on the degree of overlap and strength of bonding between the individual chains. These materials are uniformly considered to be quasi-one-dimensional owing to their chain structure but such a sweeping generalization can be too restrictive (see Materials section). Examples of this group would be NbSe$_3$, o-TaS$_3$, and NbSe$_3$.

The TMD compounds possess the chemical formula MX$_2$. The basic structural unit consists of a close-packed layer of transition metal atoms sandwiched between two close-packed layers of chalcogen atoms. The bulk crystals are fashioned from the stacking of these sandwiches which remain bonded together through weak van der Waals forces. Such materials present themselves as layered compounds and are conveniently thought of as quasi-two-dimensional. Members of this class include 2H-TaSe$_2$, NbSe$_2$ and TaS$_2$.

Both the TMT and TMD compounds present problems for the standard dilatometric techniques. The TMT single crystals may grow up to several cm in the chain direction but their cross-sections rarely exceed 10 microns x 1000 microns. Compressional forces brought to bear by optical flats and the like in a chain axis measurement would cause them to bend into arcs and even break (figure 1.2(a)). The prospects of measuring their dilation in this manner are negligible. In the case of the TMD crystals much larger cross-sections may be realized. However, for measurements in the basal plane the load-bearing edges are prone to yield, separate and flake due to the weak bonding between layers (figure 1.2(b)). The interpretation of dilatometric data under these conditions is
likely to raise questions at the very least.

Here then is the motivation for the work described in this thesis. Owing to their physical structure little or no reliable information is available concerning the thermomechanical, or electrostrictive properties of these TMT and TMD compounds.

This gap in the experimental description of these compounds retards the progress of theoretical models. Just three aspects of this are considered here: (i) the estimation of the thermal expansion tensor and the associated anisotropic Gruneisen tensor; (ii) the dilatometric character of the CDW phase transition; and (iii) the structural and elastic effects of electric fields in excess of threshold.

For compounds such as the TMT and TMD groups the high degree of crystalline anisotropy requires a more complex thermomechanical description. The definition of the vector thermal expansion coefficient must give way to a thermal expansion tensor,

\[ \alpha_{zz} = \frac{\partial e_{zz}}{\partial T} \quad (2) \]

where \( e_{zz} \) is the infinitesimal strain tensor in the crystal. The knowledge of the absolute thermal expansion tensor as a function of temperature is an important step in the estimation of the directional dependence of the force constants and the lattice vibrations. Under certain circumstances the nature of the temperature dependence can make it possible to distinguish between lattice, electronic and
Figure 1.2 (a) Dilatometer compression of quasi-one-dimensional compounds (b) compression of quasi-two-dimensional compounds.
even magnetic contributions to the expansion.

The associated definition of the anisotropic Gruneisen tensor follows,

\[ \gamma_{ij} = \frac{C_{ijrs} \alpha_{rs}}{\rho C_v} \]  

(3)

where \( C_{ijrs} \) are the components of the stiffness tensor of the crystal, \( \rho \) is the density and \( C_v \) is the specific heat at constant strain (or volume) [1.8]. The Gruneisen tensor is a measure of the anharmonic contribution to the force constants in the lattice through the variation of the mode frequencies with volume changes. It is also separable (at low temperatures) into lattice, electronic and magnetic contributions.

These two parameters bear directly on the microscopic description of the CDW compounds in their "normal" or "background" state. The elucidation of the ordinary behaviour of these materials, though often overlooked, is considered crucial to the proper understanding of the Peierls state and the approaches to it [1.9]. The instrument developed in this work cannot claim to be able to measure the complete thermal expansion tensor of the TMT or TMD compounds. Rather, it solves the problems surrounding just one of these measurements and so brings the full description that much closer to completion.

Naturally, it is the transition to the Peierls state that makes these materials so interesting from both a theoretical and practical point of view. The measurement of the thermal expansion in the region of the CDW phase transition is able to provide a route to the theoretical understanding of this system. It has been
suggested that within the simplified linear chain model outlined above that the phase transition is second order. Under this assumption the thermal expansion, the specific heat and the elastic compliance will possess discontinuities at $T_c$ which are thermodynamically linked to the uniaxial stress derivative of the transition temperature through the anisotropic Ehrenfest relations [1.11],

$$\Delta \alpha_i = \frac{-\Delta s_{ii}}{T_c} \left[ \frac{d(\ln T_c)}{d\eta_i} \right]^{-1} \quad (4)$$

and,

$$\Delta C_p = \frac{\Delta s_{ii}}{T_c} \left[ \frac{d(\ln T_c)}{d\eta_i} \right]^{-2} \quad (5)$$

where $\alpha_i$ is the thermal expansion in the $i$ direction, $C_p$ is the specific heat at constant pressure, $s_{ii}$ is a component of the elastic compliance tensor (in reduced notation), and $\eta_i$ is the component of the stress in the $i$ direction. The question of whether or not these relationships are obeyed is of considerable import to the theoretical models and to the experiments themselves. The case of NbSe$_3$ exemplifies these concerns. Measurements of the specific heat anomaly [1.10] and the stress derivative of the transition temperature [1.11] have been made for this substance. Together they predict discontinuities in the elastic compliance at both its phase transitions, 144 K and 59 K. Measurements made by the Barmatz vibrating reed technique have recorded an anomaly in the longitudinal compliance
at 144 K but no such anomaly at 59 K [1.12]. The Ehrenfest prediction for the 144 K anomaly is too small by a factor of 4 while the 59 K prediction is completely erroneous.

The question which faces the theorist is whether or not to discard the Ehrenfest relations altogether or to raise questions over the experimental technique used to gather these results. The addition of thermal expansion data can aid considerably in this matter. If the discontinuity in the thermal expansion is consistent with two other measurements then the Ehrenfest relations may stand and attention can be focused on the third experiment which appears anomalous. If no agreement can be found then a new approach must be considered.

This latter case is now all the more interesting with the advent of new treatments of the CDW transition from a fluctuation point of view [1.13]. Discontinuities in the elastic moduli of CDW systems near the phase transition have been likened to a magneto-elastic situation on the basis of specific heat anomalies [1.14]. A recent paper has treated the thermal expansion of "blue bronze" (K$_{0.3}$MoO$_3$) under the assumption of a three dimensional X-Y model [1.15]. The results obtained are not conclusive but neither are they inconsistent with this model. That fluctuations exist in these systems of low effective dimensionality can hardly be disputed but the extent of their importance to the phase transition has been a matter of conjecture in the past. This is an aspect of their behaviour which may be approached through high resolution thermal expansion measurements on both the TMT and TMD compounds.
To complete the motivation for these experiments the dramatic electric field-dependent effects experienced by the quasi-one-dimensional TMT compounds are considered from a dilatometric position. It is by now well known that the quasi-one-dimensional CDW materials exhibit ohmic or linear resistive behaviour only up to a certain threshold electric field. Beyond this value a second channel for electrical conduction is opened and the resistivity falls abruptly (figure 1.3(a)). A similar situation exists for many other physical properties including, interestingly, the longitudinal elastic modulus (figure 1.3(b)). A host of theoretical explanations has been advanced to treat the conduction-related behaviour [1.16, 1.17, 1.18, 1.19] but few of these are extended to include elastic effects and in many cases it is unclear how such an extension might be brought about.

Additional complications have also been revealed by the examination of the elastic response of o-TaS$_3$ to an AC driven CDW from 100 Hz to 1 MHz [1.20]. These experiments show that the softening experienced by the sample is sensitive to the frequency as well as the magnitude of the electrical bias beyond threshold.

The genesis of this elastic softening is still a matter of some debate. The contemporary theoretical treatments are conveniently resolved into two categories. It is the contention of some theories that the non-linear or 'sliding' CDW state is simply a softer mechanical state than the stationary CDW [1.21, 1.22]. This is ascribed, for example, to the removal of the gap in the phason spectrum when
Figure 1.3 (a) Non-Ohmic effects above the threshold electric field in Dalhousie sample of $\alpha$-TaS$_3$.

Figure 1.3 (b) Elastic softening above threshold for $\alpha$-TaS$_3$ (after reference 1.24)
then CDW begins to slide [1.23].

The second camp prefers to think that the motion of the CDW allows certain strain-coupled degrees of freedom to relax on the time scale of the elastic oscillations (which are inevitably part of the modulus measurement in the Barmatz vibrating-reed technique). The stationary state prevents this relaxation and so appears stiffer [1.24, 1.25].

In order to subject these theories to an experimental test it has become necessary to extend the longitudinal modulus measurements to the very low frequency regime [1.26]. This fills in a crucial portion of the response function where the various theories expect quite different behaviour. Quite recently, measurements of this nature were attempted which pushed the lowest frequency attainable to less than 0.1 Hz [1.27]. These have been interpreted as being in accordance with the phase relaxation models proposed above [1.25].

In this work the dilatometric technique used is adapted to measure the changes in the longitudinal Young's modulus in the static or zero frequency regime. The results obtained for o-TaS₃ agree with the trend of the more recent work in this regard with the additional observation that the crossing of the threshold field does not alter the sample structurally in any way. This last result is a further confirmation of some very early synchotron X-ray work which first placed upper limits on the possible lattice changes in the sliding state [1.28].

In the second chapter the details of the construction and operation of the apparatus are given together with the calibration results. The third chapter
describes the structure and properties of the compounds investigated with this instrument. The fourth chapter reports the "passive" thermal expansion results obtained on 2H-TaSe$_2$ in the vicinity of the CDW phase transition. These were used as a test of the instrument's capability. The thermal expansion coefficients obtained in the chain direction for NbSe$_3$ and o-TaS$_3$ are presented in chapter five. These results were obtained by the "active" dilation technique and are centred about the CDW phase transitions in these materials. The sixth chapter reveals the structural changes associated with the threshold electric field in both TMT compounds examined here. In the present circumstances upper limits on the static changes in the longitudinal elastic compliances are estimated for electric fields up to ten times threshold. The conclusions are given in chapter seven.

In the appendix may be found electrical response results for o-TaS$_3$ in very large electric fields. These are interpreted as supporting the existence of an "internal degree of freedom" in this compound's CDW state.
Chapter Two Apparatus

A solution to the experimental difficulties posed by samples that are mechanically weak is detailed in this chapter. The kernel of the solution lies in the monitoring of the length changes in the sample by other than mechanical means. In this case the exponential dependence of single electron tunnelling on the vacuum-gap distance serves as a basis for such a scheme. However, this might easily be replaced by a laser-interferometer technique as outlined at the end of this chapter.

The tunnelling dilatometer (TD) is in essence a capacitance dilatometer which employs electron tunnelling in a negative feedback mode rather than direct mechanical coupling to alter the distance between two reference planes. The reference planes here are the upper and lower plates of a (tilted-plate capacitor 1) which monitors displacement by means of an AC capacitance bridge. The use of electron tunnelling substantially reduces and in principle could eliminate the stress placed on the sample by a conventional dilatometer.

The TD may be operated in two fashions: the Tip mode and the Cantilever mode. The use of either mode is dictated largely by the structural properties of the sample under consideration. The tip mode is suitable for all but the weakest of samples while the cantilever mode places no restrictions at all on sample strength. The principle of each technique is outlined in the following paragraphs.
2.1 Principle of Operation

2.1.1 Tip Mode

The tip mode is shown in schematic form in figure 2.1. In order to measure the dilation of the sample (S) it is first mounted in a barrel (B) which may be advanced vertically by a rough approach mechanism (RA). The sample is assumed to be conducting and is electrically isolated from the frame of the dilatometer (F). The sample is electrically biased with respect to a well-cleaved section of highly oriented pyrolytic graphite (HOPG) which, though affixed to the guard-ring (GR) of the lower capacitor plate (CL), is similarly isolated from the frame of the apparatus. The barrel is advanced by the rough approach and so carries the sample's tip close enough to the HOPG surface to initiate electron tunnelling. At this point the piezoelectric actuator (PA) is brought into play as part of a negative feedback system which moves the guard-ring and lower plate so as to maintain a constant tunnelling current between the sample tip and HOPG surface. A constant current with tip-to-surface conditions unchanging implies a constant gap between the two. A length change on the part of the sample is compensated for by the action of the piezoelectric actuator receiving instructions from the feedback circuit. The motion that this entails is monitored by the separate capacitor system through an AC capacitance bridge.

The surfaces in all but ultra-high vacuum (UHV) conditions will inevitably be plagued by impurities. In a low temperature system these will be added to by condensing volatiles such as air-borne oils and moisture. No true vacuum gap will
Figure 2.1 Diagram of the Tip mode configuration
exist under these conditions and a sample will have to overcome by mechanical means the barriers placed in its path. This eliminates the possibility of using the weaker ribbon or whisker materials as tips in this mode since they will be deformed by this requirement [2.2].

2.1.2 Cantilever Mode

Apart from the details of the sample mounting the cantilever and tip modes share precisely the same features. In the case of the very weak ribbons of NbSe$_3$ or whiskers of o-TaS$_3$ the object is to avoid the mechanical deformation of the sample. This is accomplished by reversing the demand and replacing a compressive force by an extensive one. In figure 2.2 the sample (S) is shown fixed between a gallows (GA) and a cantilever (CA), the latter being mechanically biased to apply a small, controlled amount of uniaxial strain to the sample. This ensures that the sample remains straight, undeformed and that any length changes it undergoes are communicated directly to the small flake of HOPG attached to the cantilever.

This time the barrel (B) carries a tunnelling tip which is advanced into tunnelling range by the rough approach mechanism (RA). The onset of electron tunnelling brings the piezoelectric actuator (PA) into a negative feedback loop controlled by the condition of constant tunnelling current. Again, length changes on the part of the sample are reflected in piezoelectric actuator motion and measured by the separate capacitor plate system (CL, CU) as one arm of a
Figure 2.2 Diagram of the Cantilever mode configuration
capacitance bridge.

The cantilever mode confers several advantages. It ensures the stability of weak samples studied by this dilatometric technique. In addition, controlled amounts of uniaxial strain may be applied by the cantilever in order to study the elastic properties of these materials in the static regime, in contrast with vibrating-reed measurements [2.3]. Finally, this sample mounting technique allows the application of electrical leads without any disturbance to the dilatometric measurements. The only drawbacks are that samples must undergo some small uniaxial strain so that these measurements are never truly strain-free. Also, the presence of stress on the samples means that care must be taken to distinguish between structural dilation and longitudinal elastic compliance changes. This is because while the sample is under a uniaxial strain any elastic compliance changes that it undergoes will be translated into length changes.

The addition of a capacitance cell to monitor displacement may appear to be superfluous in a system which includes a piezoelectric actuator. If the studies were confined to a single temperature the capacitance cell would be redundant. However, this system was designed to operate over large temperature ranges for thermomechanical measurements. The piezoelectrically active ceramics that the actuator elements are composed of typically have very strong temperature coefficients. This in itself is not a difficulty so long as it is well-characterized. On the other hand, these materials are sensitive to their mechanical, thermal and electrical history owing to domain formation. Hysteretic behaviour is likely to be
the rule for such materials and consequently they are unsuited to a direct measurement of expansion. To this may be added the complicated properties of the epoxy glues that fix the piezoelectrics to the dilatometer frame. These are apt to change over time offering very different elastic behaviour depending on temperature and moisture conditions. In sum, these considerations force a separation of the feedback mechanism from the displacement monitoring scheme. In the system used here the feedback system, once activated, could be forgotten while the dilation was measured by standard techniques. This simplified the application of the TD immensely.

2.2 Apparatus Description

A detailed description of the experimental apparatus may be conveniently broken into four parts. These would include the mounting of the sample under study, the capacitance cell used to monitor displacement, the piezoelectric actuator used to close the negative feedback loop and finally the rough-approach mechanism required to bring tip and surface close enough to activate the feedback circuitry.

2.2.1 Sample Mounting

There are, as mentioned previously, two possible configurations for the mounting
of samples under study. These are the Tip mode and the Cantilever mode. Aside from these differences and some variations in computer monitoring all experiments described herein share exactly the same apparatus.

(a) Tip Mode Configuration.

In this mode the sample plays the role of the tunnelling tip. This is either in combination with some conventional material such as ground tungsten or on its own, providing it possesses the appropriate mechanical and electrical properties. The sample (S) is carried in a split barrel (fig. 2.3(a)) and is electrically isolated from the barrel with mica or mylar (M) as shown. The two halves of the barrel clamp together with screws so that the 'active' region of the sample's expansion begins as it exits the barrel.

Figure 2.3(b) shows the sample barrel (SB) riding in a V-groove (VG) held in place by a phosphor-bronze spring (SP). This V-groove forms part of the upper capacitor plate's guard ring. The surface into which the electrons from the sample tip (S) tunnel is formed from a small piece of highly-oriented pyrolytic graphite (Union Carbide) cleaved in the basal plane typically 3 to 5 mm square (G). The HOP graphite is glued to an insulating layer of mica (M) which is glued to the upper surface of the lower capacitor plate (CL). The negative feedback loop is closed by the piezoelectric actuator (PA) which is capable of moving the lower capacitor plate up and down. The HOP graphite is usually no more than 200 microns thick and contributes less than 10% to the overall expansion of the cell.
Figure 2.3 (a) Split sample barrel
Figure 2.3 (b) Detail of sample barrel environs
This arrangement can accommodate samples 3 mm in 'active' length, 5 mm in width and 1 mm in thickness. As alluded to previously, this mounting configuration is suitable only for samples that possess enough lateral rigidity to allow the tip to break through surface impurities present on both tip and surface. This mode of sample mounting was investigated and yielded satisfactory results on the more robust materials such as 2H-TaSe$_2$. However, the stiffness demands did give this configuration a rather limited scope. Added to this was the requirement that the sample be conducting and that a simultaneous measurement of electrical properties was not possible under these conditions. All these considerations meant that the most useful data was gathered with the alternative technique, the cantilever mode.

(b) Cantilever Mode Configuration.

In this mode the sample and the tunnelling tip are distinct from each other. The cantilever frame is shown in figure 2.4 as a horizontal plate (HP) connected to a vertical gallows (VG). The cantilever (C) is fashioned from a loop of molybdenum wire (either .002" or .004" o.d.) or by a strip of .005" phosphor-bronze roughly 1 mm wide. Each was fixed in place on the horizontal plate with a screwed-down clamping plate (CP). The sample (S) was attached to the electrically insulated end of the cantilever loop using a cyanoacrylate glue. The free end of the sample was then gently pulled upwards to be glued to the electrically insulated top of the vertical gallows. A mechanical bias between 25
Figure 2.4 Detail of cantilever frame and environs
and 150 microns applied to the cantilever ensured that the sample was always in direct mechanical communication with the cantilever. The cantilever frame was then fixed to the flexible lower capacitor plate (CL) with some GE 7031 varnish.

Of the two levers used in these experiments the phosphor bronze strip was found in the main to be superior. This was attributed to the lateral stability displayed by the continuous strip. This lateral strength enabled the cantilever to resist the torques applied to it by the tunnelling tip and so improve its mechanical stability. The molybdenum wire loop was more easily twisted by these torques and these led to anomalous dilation effects particularly over long temperature ranges.

The tunnelling system was made up of a .010" o.d. Tungsten wire (T) ground to a point at one end and mounted in the sample barrel shown in figure 2.2(a). The barrel (B) rode in a V-groove and was advanced with the rough-approach mechanism (RA). The surface into which the electrons from the tip tunnel was made of a 3 mm square flake of HOP graphite (G) glued to, but electrically isolated from the cantilever. Electrical connexion to the HOP graphite was made by means of a 25 micron o.d. gold wire lessening the mechanical loading of and vibration coupling to the cantilever. Again, the feedback loop was closed by the piezoelectric actuator (PA) which was capable of moving the flexible lower capacitor plate up and down.

This mounting technique was suitable for all types of samples and could accommodate samples of length up to 8 mm, width 6 mm and thickness 1 mm. It was particularly suited to the measurement of the expansion properties of the
quasi-one-dimensional compounds [2.4] such as the Transition-Metal Trichalcogenide, NbSe$_3$.

2.2.2 Piezoelectric Actuator

In order to close the feedback loop and move the flexible lower capacitor plate in response to length changes in the sample under study it was necessary to employ a piezoelectric actuator of large range and short response time. The device used here was the dual electrostrictive ceramic tube arrangement shown in figure 2.5. The actuator was constructed of two concentrically arranged piezoelectric ceramic tubes [2.5]. The outer tube (OT) was 1" long, .353" in diameter with a wall thickness of .020". The nominal sensitivity of this tube was 10 nm/Volt along the axis with a full range of 5 microns at room temperature. The inner tube (IT) was 1" long, .250" in diameter with a wall thickness of .020". It was made of the same material as the outer tube and had the same sensitivity and range at room temperature. The inside and outside surfaces of the tubes were coated with a nickel conductor in order to allow them to be electrically biased.

The tubes were mounted so as to compensate each other for their thermal expansion while effectively combining their sensitivities. The inner tube bore against the flexible lower capacitor plate (CL) through a top cap (TC) and rode on a brass platform (P) carried by the outer tube. The outer tube was in turn
Figure 2.5 Piezoelectric actuator mounting
carried by the movable housing (H) which screwed into the frame of the experimental cell. All joints were made fast with 5 minute Epoxy [2.6] and electrical connexions were made with .003" o.d. copper wire and Silver Paint [2.7]. The completed unit, attached with epoxy to the flexible lower capacitor plate, had a room temperature range of about 12 microns which fell to 2.5 microns at 77 K and further to 0.12 microns at 4.2 K. This latter figure must be approached with caution as the epoxy glue used to bond the piezoelectric tubes to the dilatometer frame was prone to failure at liquid Helium temperatures. Moreover, this low sensitivity did not agree with the experimental determinations made for this compound [1.29].

2.2.3 Capacitance Cell

The displacement sensor for the dilatometer relied on the measurement of the capacitance of a pair of metal plates, one of which was fixed and one which was free to move. The arrangement is shown in figures 2.6(a) and 2.6(b). The fixed upper capacitor plate (UCP) was a cone-shaped piece of metal wrapped in .0005" mylar and glued into a large guard-ring (GR) which formed part of the frame of the device. The flexible lower capacitor plate (LCP) was another cone-shaped piece of metal wrapped in mylar and glued into a cantilever tongue (CT) weakened at the pivot by a cut-out (CO). Both upper and lower plates and mountings had their active surfaces polished flat to within 1 micron using a
Figure 2.6 (a) Cross-section through capacitance cell
Figure 2.6 (b) Upper and lower capacitor plates with guard-rings.
diamond paste suspended in oil [2.8]. The flexible lower plate was sandwiched between the upper plate’s guard-ring and a tripod frame (TF) which carried the piezoelectric actuator (PA). A portion of the upper plate’s guard-ring was milled away (MA) to allow access to the cantilever tongue for the mounting of either an HOP graphite surface or a cantilever gallows as described above.

The dimensions of the plates and their rest separation were chosen with a view to maximizing the sensitivity while minimizing the effects of airborne dust contamination of the plates. The upper plate was 10 mm in diameter, the lower plate being somewhat larger to minimize the effects of fringing fields in conjunction with the upper plate’s guard-ring [2.9]. The rest spacing was calculated from the capacitance to be roughly 60 microns. The sensitivity to displacement was approximately 0.1 pF/μm which allowed estimates of dilation on the order of 0.1 nm to fall within the Johnson noise of the capacitance bridge.

It was originally imagined that shims would be required between the upper and lower capacitor plates to ensure a minimum rest spacing. This proved to be unnecessary due primarily to the strain-induced flexing of the cantilever tongue when sandwiched between the upper plate’s guard-ring and the tripod frame. When the system was bolted together the stress applied by the bolts was relieved by the apparatus by flexing the free portions of its makeup - in this case, the cantilevered tongue carrying the lower capacitor plate.

The capacitance cell so formed is of a tilted-plate design as described by Brandli and Griessen [2.10]. The relationship between capacitance and displacement has
the usual inverse form, 

\[ C = \frac{2 \pi e_0 b^2 (1 - \sqrt{1 - (\frac{r}{b})^2})}{d} \]  

(1)

where \( b \) is the distance from pivot to plate centre, \( r \) is the plate radius, \( d \) is the plate spacing at their centre and \( e_0 \) is the permittivity of free space (figure 2.7).

The capacitance cell was calibrated with a commercial micrometer [2.11] which bore against the cantilever tongue in precisely the same position as the piezoelectric actuator. The results of this calibration are given in figure 2.8 and agree with those calculated from equation 1 to within 1%.

The force constant of the cantilevered tongue defined by the cut-out was a compromise between mechanical stiffness against vibration and the ability of the piezoelectric actuator to move the lower plate. The calculation was based on the maximum force that the cantilever could apply to the piezoelectric tubes described previously. This force would necessarily deform the tubes and was constrained to be 10% or less than the maximum displacement of the tubes when electrically biased. The figure of 10% was chosen as a coarse rule of thumb to limit the amount of non-electrostrictive distortion suffered by the piezoelectric actuators. This led to a cut-out which gives the cantilever tongue an effective force constant of 0.1 N/micron. This stiffness was required to reduce the effect of coupled-in
Figure 2.7 Diagram of tilted-plate capacitor
Figure 2.8 Calibration of capacitance cell with micrometer
vibrations at the level of the electron tunnelling on the cantilever tongue. The resonant frequency of the cantilever in free vibration was greater than 10 kHz and the entire system was much more rigid still when the piezoelectric actuator was fixed in place.

2.2.4 Rough Approach Mechanism

In order to establish electron tunnelling it was necessary to arrange that the tunnelling tip and the graphite surface be within the range of the piezoelectric actuator at the temperature that the approach is made. The mechanical system devised for this task was employed in two stages.

In the first stage a coarse approach was made under a x40 microscope at room temperature to bring the tip and surface to within 10 microns of each other from a starting gap of 1 to 2 mm. This was done with the aid of an expanding approach barrel shown in figure 2.9(a). This barrel came in two parts connected by a threaded screw (TS) and lay in the V-groove (VG) of the rough approach mechanism held in place by springs (SP).

The upper barrel (UB) was tapped to 24 tpi and could not move up or down being restrained by the pin of the fine approach barrel shown in the subsequent figure 2.9(b). The lower barrel (LB) could move up and down and was tapped to 32 tpi. Its lower surface bore directly against the sample barrel (SB) which
Figure 2.9 (a) "Expanding" coarse approach barrel
Figure 2.9 (b)  Rough approach mechanism in cross-section
carried the tunnelling tip (T). The threaded screw was threaded 24 tpi above the
knurled ring (KR) and 32 tpi below. One full turn of the threaded screw would
advance the sample barrel by 265 microns and allowed positioning to within 5
microns. Once in position the approach barrel was made rigid by the freezing of
vacuum grease [2.12] (smeared over the threads) at the liquid nitrogen
temperatures it was designed to operate at. Backlash eliminated the possibility of
using lock nuts.

The fine approach mechanism was also a differential screw design and is
illustrated in figure 2.9(b). The device was constructed so as to be as rigid as
possible to reduce the effect of vibrations. The approach barrel (AB), now rigid
at low temperatures owing to the freezing of the vacuum grease on its threads, lay
in a V-groove (VG) held in place by springs. A floating barrel (FB) with a pin
(P) rested in a circular hole and was kept in contact with a threaded screw (TS)
by means of a helical spring (HS). The threaded screw had a metric thread 8 x
1.25 mm for the floating barrel which changes to 20 tpi in order to screw into the
base of the rough approach body (B). One full turn, by means of a mechanical
feed-through, advanced the pin which is in contact with the approach barrel by 20
microns. Its full range was 0.2 mm and was enough to bring the tip and the
surface to within the range of the piezoelectric actuator at 77 K.

In actual fact the motion in one full turn was closer to 50 microns as checked by
a travelling microscope. Clearly the design tested the limits of the machine tools
used in its fabrication. However, with care it proved serviceable in these
2.2.5 Probe  (figure 2.10)

The capacitance cell (C) with the piezoelectric actuator mounted in position was firmly bolted to the underside of a metal platform (PT) suspended from four stainless steel tubes. To the top of the platform was mounted the rough approach mechanism (RA) in such a way as to have the axis of the approach barrel (AB) coincide with the axis of the sample barrel. In this way torques were avoided as the two bore against each other.

A mechanical feed-through (MF) allowed the adjustment of the rough approach when the system was cold and evacuated. Electrical feed-throughs rose through stainless steel tubes which also served as vacuum lines. The tubes were soldered to a top plate which seals against the mounting ring of the liquid helium dewar to allow helium gas recovery. Electrical, mechanical and vacuum connexions were made at the top which remained at room temperature.

When the inner can (IC) was sealed to the inside flange (IF) with Wood's metal the sample space so formed could be evacuated and replaced with helium exchange gas. The inner can also carried a non-inductively wound resistance heater on its outer surface to allow temperature control in the experiment. Over the inner can the outer can sealed against the outer flange with Wood's metal. The heater space so formed could also be evacuated and replaced with helium experiments.
Figure 2.10 Diagram of experimental probe
exchange gas. The pressure in the sample space could be reduced by rotary pump alone to 60 microns of mercury at room temperature. Further reductions in pressure were possible by diffusion pumps and cryo-pumping techniques.

2.2.6 Cryostat (figure 2.11)

The probe (P) was fitted inside a glass liquid helium dewar (HD) and sealed against its mounting ring with its top plate. In order to minimize the transfer of vibrations from the building into the experiment the helium dewar with the probe mounted in it was suspended from the concrete ceiling (C) of the laboratory by three elastic cords (EC). The fully loaded helium dewar extended this elastic system by approximately 50 cm from its unstrained position. This gave the suspended dewar a resonant frequency of 0.7 Hz. This was sufficiently far from the peak in building vibrations at 20 Hz [2.13] to make this an effective low pass mechanical filter for the reduction of coupled-in building vibrations. To further reduce these vibrations all vacuum lines were disconnected before an experiment was begun and all electrical connexions were made with a narrow gauge coaxial cable approximately 2 mm in diameter.

When fully loaded the helium dewar was arranged to be 1" from the bottom of the empty liquid nitrogen dewar (ND) in which it rested. Care in alignment ensured that the helium dewar did not bump into the walls of the nitrogen dewar. The outer dewar rested on a platform of sandbags (SB) to reduce the coupling of
Figure 2.11 Diagram of cryostat mounting with vibration isolation.
building vibrations through the liquid nitrogen into the experiment. The observation of regular, stable tunnelling in this experiment demonstrated the effectiveness of the techniques described above in eliminating a serious source of vibration error. In preliminary experiments without such vibration isolation the merest foot-fall was enough to drive the tip into the surface and so begin a noisy and unstable tunnelling response due, no doubt, to debris from the ruptured surface coating the tip. Operation without the vibration isolation was never practical.

2.2.7 Electronics

There are several different experiments described in this work. However, they all share the same electronic elements of the Tunnelling Feedback Circuit, the AC Capacitance Bridge and the Temperature Sensor. Differences arise in the inclusion of AC techniques for measuring slope resistance as a function of electric field and in the specifics of computer data logging and/or control of experimental parameters.

(a) Negative feedback circuit

The tunnelling feedback circuit shown in figure 2.12 uses the principle of integral feedback to stabilize the detected electron tunnelling current between the tip and
the graphite surface. Implicit in this arrangement is the exponential dependence of the tunnelling current $I$, on the tip-to-surface distance, $s$,

$$I = A V e^{-bs}$$

(2)

where $A$ is a constant, $V$ is the voltage bias of the graphite surface and $b$ is related to the effective work function between the tip and the surface.

The graphite surface is biased with respect to ground by a regulated voltage divider powered by batteries or by an ac/dc power supply. Electrons tunnelling out of the tip (T) across the gap into the surface (S) are collected by a pre-amplifier which is battery operated to reduce the amount of line noise present in the raw current signal. The current signal is converted into a voltage signal with the proportionality of $1 \text{ mV}/\text{Na}$. Connexions from the tip to the pre-amp are made as rigid as possible to minimize the Triboelectric contributions to the current. The pre-amp is attached to the room-temperature end of the probe to reduce the path between it and the tunnelling tip in an effort to further reduce interference. The operational amplifier upon which this design is based is an AD611JH dual FET input op-amp with a low input bias and offset currents [2.14].

The voltage signal generated by the pre-amp is sent to an AD522 Instrumentation amplifier [2.14] with a fixed gain of 100 and a CMRR greater than $130 \text{ dB}$. This boosts the signal to $100 \text{ Mv}/\text{Na}$. From here it is necessary to linearize the response of the circuit to gap distance changes. The use of two diodes (1N4148) in the feedback of an operational amplifier creates a quasi-
Figure 2.12 Negative feed-back tunnelling electronics.
logarithmic amplifier of bi-polarity. The basic advantage of this design over monolithic units is cost. The disadvantage lies chiefly in the lack of temperature compensation for the device. For the conditions under which these experiments are performed this is not too severe. Taking a typical model for diode response as a function of temperature [2.15] one may expect set-point fluctuations of less than 0.05 Na/K. The effective work functions present in the 'dirty' conditions of these experiments are quite small (< 0.1 eV) leading to an estimate of less than 0.02 nm/K for the temperature-induced fluctuations in position. Thus, variations in laboratory temperature are not expected to contribute above the background electrical noise of the experiment.

The linearized signal is delivered to the summing amplifier where it is subtracted from a user-defined set point. The error signal is then integrated with a user defined time constant (between 1 msec and 1 second) and amplified by an operational power supply [2.16]. The operational power supply (OPS) then drives the piezoelectric actuator (PA) to close the feedback loop.

(b) **The capacitance bridge**

Variations in the gap spacing of the tilted-plate capacitor are reflected in the capacitance of this cell. These capacitance variations are detected by means of an AC Capacitance Bridge [2.17] with a lock-in amplifier [2.18] acting as the null detector. The Johnson Noise in the capacitance bridge limits the absolute
determination of capacitance and hence displacement. The input impedance of the bridge (99.7 kohm) and the bandwidth of the lock-in amplifier (typically at 300 msec) leads to a lower sensitivity limit of about 0.3 nm or one part in ten million for the smallest samples used in these experiments.

When measurements are taken with this system the conversion to capacitance from the out of balance voltage is taken as almost linear. The real part of the voltage change in this transformer-type AC bridge [2.19] is directly proportional to the change in capacitance with second order corrections of less than 1% for the capacitance range used here. The null detector signal is measured directly with either an X-Y recorder or a digital volt meter (DVM) monitored by a computer.

(c) Temperature measurement

The calculation of thermal expansion relies as much on the accuracy of the thermometry as on the estimation of displacement. The temperature of the sample is measured using a semiconducting diode element [2.20] with a fixed excitation current. The rated absolute accuracy of the calibration curve supplied by the manufacturer is within 0.1K. The stability and reproducibility of the device allows differential estimates in the range of 5 mK. A conversion from diode voltage to temperature is accomplished by linear interpolation of the supplied calibration data. The sensor itself is not in direct contact with the sample but rather is mounted on the side of the rough approach unit with GE 7031 varnish.
The guarantee of thermal equilibrium, not only between sample and thermometer, but throughout the experimental cell is of the very greatest importance in thermal expansion measurements. This is due to the differential nature of expansion measurements in which the dilation of the sample is compared to that of the cell. In early experiments thermocouples were placed at the outside surface and in the centre of the probe and the thermal gradients measured between the two. The sensitivity, however, was not great enough to permit an accurate estimation of their importance. Rather, in subsequent calibrations (mentioned below in this chapter) it was found that the greatest rate at which the temperature of the cell could be changed and still avoid thermal gradients was about 4.5 K/hr. This came from reproducibility tests carried out during the calibration experiments which varied only the rate at which the sample was warmed.

(d) Differential resistance measurement

In some experiments the measurement of expansion was carried out simultaneously with the measurement of the sample's differential resistance. The measurement of differential resistance is made by the detection of the AC component of the current through a sample under the influence of an AC voltage excitation which is carried on top of a DC voltage sweep. The differential resistance is then the ratio of the AC voltage amplitude to the detected AC current amplitude.
Figure 2.13 Differential resistance electronics.
The circuit diagram in figure 2.13 shows the principle features of this technique. The sample itself is mounted in a four-wire resistivity configuration. The DC voltage across the sample is measured by a high-impedance DVM. The AC voltage signal is externally generated providing both the AC voltage excitation for the sample and the reference signal for the lock-in amplifier's phase-locked-loop. The DC voltage level is generated by means of an analog integrator, a commercial signal generator or a digital-to-analog converter (DAC) controlled by a computer.

The DC voltage ramp is buffered and then added to the capacitively-coupled AC excitation. The summed signal is given to a power supply/amplifier [2.21] in order to overcome the current sourcing limitations of the LM741 operational amplifiers. The current-amplified signal is then fed into the sample via a 10 ohm current-sensing resistor. The AC voltage across this resistor is measured by a lock-in amplifier running in a differential mode [2.22]. The differential resistance of the sample is calculated,

\[ R_{\text{diff}} = R_{\text{sense}} \left[ \frac{2}{\pi} \frac{V_{\text{ex}}}{V_{\text{lockin}}} - 1 \right] \quad (3) \]

where \( R_{\text{sense}} \) is the sense resistor value. The factor of \( 2/\pi \) arises from the integration of the modulated signals performed by the lock-in amplifier. In addition the the DC current response is measured with a DVM across the sense resistor. The typical excitation was less than 100 mV at 300 Hz.

With this arrangement it is possible to make simple zero-field resistance measurements in order to fix the position and width of any phase transitions that
the samples undergo. In addition, by ramping the DC voltage, studies of the non-ohmic effects or threshold fields in [2.23] the quasi-one dimensional CDW compounds may be made.

(e) Computer Control and Data Logging

A schematic diagram of the computer data logging set-up is shown in figure 2.14. In its simplest mode the computer logs only the signal from the capacitance bridge null detector and the thermal-sensing diode's voltage. Communication from the XT-type computer to the DVM's is made via an IEEE bus. If the zero-field slope resistance is required another DVM is added to the IEEE bus and minor adjustments to the computer routine are made. To make expansion and slope resistance measurements as a function of swept DC electric fields two more DVM's are added to measure the sample's DC current and voltage, the sweep signal being generated by instructions from the computer over the IEEE bus to the DAC. All the data is stored on magnetic disk.

2.3 Calibration of Dilatometer

The calibration of the dilatometer against a material of well-characterized dilation is the next logical step in its development. This is necessary as the
Figure 2.14 Diagram of computer control and data-logging.
The dilatometer was constructed from various different pieces of free-cutting brass. The use of a single well-controlled alloy would have been preferable in this case and the absence of this detail is a deficiency in this apparatus which must be overcome by calibration experiments. With a calibration that determines the "cell" contribution to the dilation the relative expansion measurements obtained can be converted to absolute quantities. In the absence of a calibration conventional dilatometric techniques may only reveal relative dilation changes in the regions of, for example, structural phase transitions.

Unfortunately, this aspect of the dilatometer's performance turned out to be particularly poor. The reason advanced for this lies in the design of the rough approach mechanism used to manoeuvre the tunnelling tip close to the HOPG surface. The evidence for this assertion is contained in the calibration curves shown in figures 2.16 and 2.17.

In the first calibration experiments the influences of the rough approach mechanism and the piezoelectric actuator were removed from the experiment. A sample of aluminum was prepared for mounting in the sample barrel as shown in figure 2.15(a]. This was brought to bear directly against the flexible lower capacitor plate and then very rigidly clamped in its v-groove figure 2.15(b). The clamping pressure used here was far in excess of that typically used in tunnelling dilatometer experiments. The leaf spring was made of much thicker material (.020" phosphor-bronze) and the sample barrel could not be moved unless the tension was relaxed. The sample barrel was completely de-coupled from
Figure 2.15 (a) cross-section of aluminum sample in split barrel. (b) aluminum sample bearing against flexible lower capacitor plate.
the expansion barrel of the rough approach mechanism in the same way that the lower capacitor plate was de-coupled from the piezoelectric actuator. This latter precaution was necessary to prevent the sample's pressure on the lower capacitor plate from damaging the piezoelectric tube assembly.

This "direct" calibration was made between 80 and 300 K with varying heating rates. The first observation was that reproducibility could only be obtained if the warming rate was reduced below 4.5 K/hr. Using this heating rate the calibration curves in figure 2.16 were obtained. The agreement is quite remarkable with the departures nearing the 3% level at the highest temperatures. This figure could no doubt be improved if care was taken to reduce heating rates in the regions where thermal gradients are likely to play the greatest role (ie. at the higher temperatures). However, for the purposes set out here these results are able to confirm that the dilatometer can be calibrated in a direct way without difficulty.

The next experiment was a copper calibration with the sample mounted in the cantilever mode and the tunnelling feedback system in operation. The copper sample was a strand of high purity copper thermocouple wire (99.99% pure) .003" in diameter and 5.79 mm long. The lever was a strip of phosphor-bronze .005" thick, 0.95 mm wide and 4.44 mm long. The mechanical bias at room temperature was 0.82 mm leading to a uniaxial stress of 100 MPa.

The results of these experiments are illustrated in figure 2.17. The litmus test of any calibration is reproducibility and it is evident that these results lack just this
Figure 2.16 Calibration of probe against aluminum sample.
Figure 2.17 Calibration of probe against cantilever-mounted copper
sample quality. It should be noted here that after tunnelling was established at 80 K the rough approach mechanism was de-coupled from the sample barrel and never again used. The tunnelling conditions as well as the warming rates were the same in each case (4.5 K/hr) and the cooling between each run was as slow as practicable.

The difference between the "direct" calibration and the cantilever experiments is that the sample barrel must be allowed to move in the latter. It is this demand which is believed to be the obstacle to a proper calibration. The sample barrel lies in a v-groove held in place by a leaf spring. In these circumstances it is possible for the barrel to move under the influence of gravity and "creep" downwards. In addition, the rough approach will cause strains to build up between the sample barrel and the leaf spring that holds it in place. The gradual release of these forces is determined in a complicated way by the frictional conditions between these two objects as well as by the temperature gradients that surround the entire system and this too leads to "creep". Finally, it is possible for the sample barrel to tilt within the v-groove and so describe arcs of motion as the stress fields are continuously altered by the ambient conditions. These effects add up to an irreproducible motion on the part of the sample barrel which occurs on a microscopic scale. This motion eliminates the possibility of calibration by preventing the realization of identical conditions for all experiments.

There is little that may be done to improve this situation so long as electron tunnelling is used as the displacement monitoring technique. There is no way
around the requirement of some kind of rough approach mechanism which inevitably asks one of the reference positions to be moved. The tunnelling tip must be brought to within a few microns of the HOPG surface before the piezoelectric actuator's range can be profitably employed. Increasing the clamping pressure would simply increase the stress fields generated by the approach unless it rendered the barrel incapable of motion at all.

The inability to calibrate the tunnelling dilatometer is a severe restraint on its capabilities. This restricts conventional techniques to the study of relative changes in the thermal expansion over temperature ranges small enough to guarantee a linear background expansion. This is the analysis applied to the 2H-TaSe$_2$ results found in chapter 4. In chapter 5, the need for a calibration is discarded altogether by the use of a "self-heated expansion" technique. This has the sample raise its own temperature by means of Joule heating. The dilatometer does not respond to this heating since the power levels are kept below several milliwatts. With the use of the sample's resistance as a thermometer the dilation and temperature changes may be correlated to reveal the expansion independently of the probe.
Chapter Three  

Materials

3.1 $\alpha$-TaS$_3$

It is usual to synthesize crystalline compounds of reduced effective dimensionality by means of the halogen vapour transport (HVT) technique. The pure components of the material to be grown are mixed in stoichiometric quantities and placed at one end of a quartz ampoule. The ampoule is evacuated, a small quantity of halogen introduced and then the ampoule is sealed. This ampoule is placed in a zone furnace whereby a fixed temperature gradient is maintained between the material's end (hot) and the crystal growth end (cooler). A convection cell of halogen vapour is driven by the temperature gradient, picking up the reacted compound at the material’s end and transporting it to the growth end where single crystals are slowly built up [3.1]. The time required to grow a sufficient quantity of crystals may vary from several days to several weeks. All the synthesized CDW compounds used in these experiments were prepared by Mr Ben Fullerton at the Dalhousie University Department of Physics.

TaS$_3$ may exist in either monoclinic or orthorhombic polytypes. When prepared above 800 C the growth of solely the orthorhombic phase is assured [3.2]. If the growth temperatures are confined to between 600 and 700 C the crystal growth is multiphase with monoclinic and orthorhombic polytypes of TaS$_3$ coexisting with
the layered compound TaS₂ [3.3]. In this case it is not unusual to find both
polytypes coexisting on in a single crystal whisker. The TaS₃ grown at Dalhousie
and used in the experiments described here was prepared from 99.9999% pure
tantalum and 99.9999% pure Sulphur. The quartz ampoule was charged with
Iodine vapour and crystals grown above 800 C to ensure uniformity of the
orthorhombic polytype. When the ampoule was finally cooled the growth end was
covered in a matted matrix of extremely fine whiskers which had adhered to the
ampoule wall. The crystals were dark and shiny with a metallic lustre. All the
whiskers were of practically uniform cross-section, between 5 x 5 microns² and 10
X10 microns². In length they ranged from one or two mm to several cm. When
manipulated individual whiskers were flexible but broke when sharply bent.

In order to verify the polytype in the ampoule, X-ray measurements at room
temperature were attempted. The orthorhombic form has not yet been fully
described but the monoclinic polytype is well known [3.4]. However, this
examination failed for lack of a sufficient quantity of the randomly oriented
powder required for the X-ray diffraction apparatus. The grinding of the strong
whiskers was both difficult and consumed a large fraction of the growth lot. The
polytype was instead identified from the position of the CDW phase transition
determined from the longitudinal resistivity measured as a function of temperature
shown in figure 3.1. The presence of a single phase transition near 220 K is
indicative of the orthorhombic form [3.5]. The monoclinic polytype has two CDW
phase transitions, one at 240 K, the other at 160 K.
The basic structural unit of all the transition-metal trichalcogenides (TMT) is a trigonal prism of chalcogen atoms (Sulphur in this case) with a single transition metal atom (tantalum) occupying roughly the centre of the prism. The prisms are stacked end-to-end to form infinite chains as shown in figure 3.2 [3.6]. Although the final crystal structure of α-TaS₃ has yet to be determined it has been suggested that it belongs to the space group Cmcm [3.5]. The unit cell is tentatively given a total of 24 formula units; a two-layer slab consisting of twelve columns [3.7]. The columns occupy a unit cell cross-section of a = 3.6804 nm by b = 1.5117 nm. The two layer dimension, the chain axis, has c = 0.3340 nm [3.5]. Though there are a large quantity of chains in the unit cell the single CDW phase transition points to the presence of a single chain type only [3.8].

In its macroscopic appearance as whiskers, as well as its microscopic structure, α-TaS₃ is a highly anisotropic compound. This aspect of its structure is no less displayed in its physical properties. Calculations indicate that α-TaS₃ has a greatly anisotropic band structure due in large measure to the strong overlap of the d-orbitals in the chain direction [3.8]. The longitudinal mean free path estimated from conductivity measurements is roughly 3 nm while the transverse mean free path is only 0.03 nm [3.9]. The unusually low figure for the transverse case suggests that diffusive rather than metallic mechanisms are responsible for electron transport between the individual chains. Large anisotropies of this nature are reflected in an almost one dimensional band structure [3.8]. The low effective dimensionality of this electron-phonon system makes it particularly susceptible to
Figure 3.1 Resistance of o-TaS$_3$ as a function of temperature.
Figure 3.2 Trigonal prisms of o-TaS$_3$ (after reference 3.6).
the soft mode, metal-insulator Peierls transition as outlined in the introduction.

For o-TaS$_3$, there is a single CDW phase transition at 220 K as shown in figure 3.1 for data obtained for the growth lot prepared at Dalhousie University. (the logarithmic derivative of resistance in figure 3.3 puts $T_c = 219.75$ K). Evidence for the formation of the CDW state is provided by low-temperature X-ray diffraction: superlattice reflections appear in the material's diffractogramme corresponding to wavevectors (2.5, 0.125, 2.25) [3.10]. This indicates a CDW in the chain direction which is either commensurate or very nearly commensurate with the underlying lattice. The commensurability parameter in this case would be 4. There is weak evidence for an incommensurate-commensurate phase transition below 160 K [3.11]. More recent re-appraisals lower the so-called 'lock-in' temperature to about 60 K based on a rise in the resistivity and its interpretation as an enhanced Fermi surface gapping by commensurate CDW structures [3.12].

It is evident that the onset of the CDW state coincides with a large rise in the resistance. This implies a transition to a Peierls insulator state with the practically complete loss of Fermi surface [3.8]. It must be noted in passing that there is a turn-over in the resistivity near 270 K where the material seems to enter a semi-metallic state, leaving behind the metallic state. This is due to the highly one-dimensional nature of this compound which tends to support strong one-dimensional fluctuations well above the CDW phase transition. This leads to a pseudo-gap formation and a resistivity rise [3.13].

The temperature dependence of the resistance below the CDW phase transition
Figure 3.3 Position of phase transition in logarithmic derivative of α-TaS$_3$ resistance.
allows the estimation of the size of the Peierls gap in the single-particle energy spectrum [3.14]. This value typically lies in excess of the anticipated BCS value, $1.75 k_b T_c$. This disparity is also attributed to fluctuations through the depression of the ordering temperature. The gap has also been measured by optical methods and found in agreement with resistivity estimations but in conflict with tunnelling data [3.15]. The CDW phase transition also induces a dip in the longitudinal Young's modulus and a rise in the internal friction calculated from vibrating-reed experiments [3.16]. These may be combined with the pressure dependence of the transition temperature [3.17] or its uniaxial stress dependence [3.18] in the Ehrenfest relations derived from the thermodynamic relations at a second order phase transition. These lead to predictions of the discontinuity in the specific heat and in the coefficient of thermal expansion. The specific heat anomaly that is suspected in this material has not yet been measured. The anomaly in the coefficient of thermal expansion is estimated for the first time in the experiments described in the Active Dilatometry chapter. It is found to be at odds with the predictions from the Ehrenfest relations.

Within the Peierls state the CDW is free to organize itself in ways which depend on its registry with the lattice. If it is truly commensurate (and the data is not sufficiently accurate to pronounce upon this) then it simply lies in a position fixed by the minimization of the commensurability energy. If incommensurate then it may just lay out of registry with the lattice or the CDW may collect in regions nearly commensurate with the lattice separated by a regular array of phase
discontinuities or discommensurations (DC). The latter arrangement is thought to be a lower energy configuration [3.19]. The question of a commensurate-incommensurate transition has been alluded to above but no firm results exist to settle the question. However, the existence of a DC lattice is supported by dark-field electron microscopy which sees large domain structures 1 micron long in the chain direction and roughly 30 nm wide [3.9]. Smaller domains exist on the 2 nm x 2 nm scale. The presence of phase solitons as these DC's might be called is also suggested by thermal hysteresis and memory effects in so far as these point to domains [3.20]. Efforts to observe any effect of electric fields on these supposed domains have been unsuccessful [3.9].

Perhaps the source of greatest interest in these materials is their electric field-dependent behaviour. In the early theoretical formulation of one-dimensional electron-phonon systems the effect of steady electric fields on the CDW was seen as the explanation for superconductivity [3.21]. Later treatments included the inevitable presence of defects and impurities leading to the prediction of non-linear conductivity above a certain threshold. These effects have been observed in a wide variety of the compounds of the TMT class. An example of this is shown in figure 3.4 taken from experiments performed on the samples grown at Dalhousie. Here the differential resistance (the local slope of the I-V curve measured by a phase-locked-loop technique) is plotted as a function of the applied electric field. Up to 100 mV/cm the material has a constant resistance, obeying Ohm's law. Beyond this threshold value the linear relationship between
Figure 3.4 Threshold electric field in α-TaS$_3$ at 112 K.
Figure 3.5 Variation of the threshold electric field with temperature for o-TaS$_3$. 
the current and the voltage breaks down as a new channel for charge transport is introduced. This result is typical of this material as is the variation of the threshold field with temperature shown in figure 3.5 [3.22]. The size of the threshold field in this sample lot is, however, extraordinarily low for this material. This is indicative of an impurity concentration in this lot of roughly $10^{17}$/cm$^3$, perhaps an order of magnitude lower than is usual. The source of these impurities would likely be found in the tantallum used in the preparation of this compound [3.22]. Various theories exist to explain these effects and these may be conveniently resolved into the semi-classical description [3.23], the macroscopic quantum tunnelling model [3.24], the gauge-invariance-pair theory [3.25] and the soliton model [3.26]. It would tax brevity to attempt to summarize them all.

Experimental evidence exists to support all these approaches and it is a chief concern of these and other experiments to distinguish the proper theory from among them.

The thermoelectric power measurements on o-TaS$_3$ show that little or no entropy is carried by the non-linear channel for conduction [3.27]. Moreover, Hall-effect experiments indicate that the non-linear component is unaffected by the Lorentz force [3.28]. Associated with the onset of non-ohmic conduction is a broad-band noise which follows the power relationship $w^{-0.8}$ [3.29]. There is also a narrow-band noise which is expressed as sharply resolved peaks in the noise spectrum of the current [3.30]. These peaks are found to be at frequencies which are proportional to a fundamental frequency. In o-TaS$_3$ the fundamental follows
the expression,

\[ f_0 = \frac{I_{CDW}}{e n_{CDW} A L_{CDW}} \]  

(1)

where \( I_{CDW} \) is the component of the overall current associated with non-linear behaviour, \( n_{CDW} \) is the density of electrons participating in the CDW, \( A \) is the sample cross-section and \( L_{CDW} \) is the wavelength of the CDW [3.31]. This form is suggestive of a semi-classical description of CDW motion, that is, uniform translation of the CDW (multiples of the fundamental are generated by the non-sinusoidal character of the CDW condensate). However, as is explained in the section on \( \text{NbSe}_3 \), this relation is not always obeyed in such an unambiguous manner.

The onset of non-linear conduction also brings a dramatic softening in the longitudinal modulus of elasticity [3.32] and in the shear modulus [3.33]. These investigations are carried out by the Barmatz vibrating-reed technique and necessarily occur at finite elastic frequency, between 100 Hz and 1 MHz [3.34]. In recent experiments at frequencies below 0.1 Hz no change in the longitudinal modulus is detected to within 2 parts in 1000 [3.35]. This result is confirmed in the elastic modulus experiments that may be found in chapter six. In these experiments the upper limit for elastic modulus changes at the threshold electric field is reduced to 21 ppm in the limit of zero mechanical frequency. The explanation of these results may serve as a basis for the evaluation of competing theories.
3.2 NbSe$_3$

The NbSe$_3$ used in the experiments described here was prepared at Dalhousie by the HVT technique mentioned earlier [3.1]. The 99.9999% pure Niobium and 99.9999% pure Selenium were combined in stoichiometric quantities and the single crystals grown with Iodine as the transporting vapour. After a growth period of 2-3 weeks the condensing end of the ampoule was covered in a dense matrix of fine crystals. In contrast to o-TaS$_3$, these were not in the form of whiskers but rather ribbons with a wide variety of cross-sections. The long axis of the crystals varied between a few mm to no more than one cm or so. In the transverse dimension the crystals seemed to form slabs of uniform thickness (perhaps 20 microns) and widely varying width, between 10 microns and one mm. This variation seemed to be due to the presence of an easy cleavage plane in this dimension. The crystals were dark and lustrous in appearance. The easy cleavage plane meant that the ends of the samples were usually frayed and often defects could be seen running parallel to the long axis caused by incomplete cleaving. This could be exacerbated by rough handling. NbSe$_3$ was as pliable as o-TaS$_3$ and even appeared somewhat softer. The defects tended to reduce the effective tensile strength.

NbSe$_3$ exists in only one crystalline form and thus the identification within the growth lot is simplified. It has also been fully indexed and its microscopic structure is completely described [3.37]. NbSe$_3$ belongs to the space group P2$_1$/m and
contains six formula units within the unit cell. In common with all members of the
TMT class the basic structural unit is the trigonal prism of chalcogens framing a
single transition metal atom as shown in figure 3.2. The monoclinic unit cell
(shown in figure 3.6) displays three distinct pairs of chains labeled I, II and III.
The dimensions of the unit cell are \( a = 1.0009 \, \text{nm}, \, b = 0.34805 \, \text{nm} \) and \( c = 1.5629 \, \text{nm} \) with the canting angle of \( 109.47^\circ \). Here the \( b \) axis corresponds to the
chain direction. The prismatic chains found along the two-fold chain axis do not
share any anion among them. In the \( c \) direction chains are linked by Nb-Se bonds
and so form slabs which are infinite in the \( c \) and \( b \) directions. The individual slabs
are held together by van der Waals bonds but the interchain Nb-Se bonds are
much stronger, being ionic-covalent. This makes NbSe\(_3\), in contrast with \( \alpha\)-TaS\(_3\),
more truly quasi-two-dimensional than quasi-one-dimensional, the prismatic chain
construction notwithstanding. This effective dimensionality is reflected in ribbon
rather than whisker formation as mentioned above. The compound synthesized at
Dalhousie has been subjected to a powder X-ray examination at room
temperature (figure 3.7) and the unit cell parameters quoted above have been
confirmed.

The effective dimensionality alluded to above in the crystal structure may also
be gauged from the anisotropy in the conductivity at room temperature [3.38].
The longitudinal (\( b \) axis) mean free path is estimated to be 9.6 nm while the
transverse mean free path is 0.96 nm. These figures suggest that band theory may
be applied in both directions. By way of confirmation, Shubnikov-de Haas
Figure 3.6 Cross-section of the monoclinic unit cell of NbSe₂. The "y" designations refer to the out-of-plane position of the atoms in units of the "b" lattice vector (after reference 3.13).
Figure 3.7 Powder X-ray diffraction results for NbSe$_3$. 
quantum oscillations reveal that the while the Fermi surface is highly anisotropic it is still three-dimensional [3.39].

With such an anisotropic Fermi surface it is not surprising to learn that NbSe$_3$ is also susceptible to a Peierls metal-insulator transition. Direct evidence for the CDW state in this compound is provided by electron diffraction experiments which report an initial superlattice formation below 144 K followed by a second superlattice below 59 K [3.40]. Further examination by X-ray diffraction shows that the incommensurate CDW below 144 K is strongly localized on the Nb(I) chains with reduced wavevector (0, 0.243, 0). The second incommensurate CDW at 59 K has reduced wavevector (0.5, 0.259, 0.5) and is found to be localized on the Nb(III) chain pairs making it independent of the first CDW [3.41]. Recently, direct evidence has cast doubt on this interpretation of the independence of the two CDW's. Using an STM on the surface of NbSe$_3$ at 4.2 K the two CDW's have been identified and positioned so that all three chain types appear to participate in the combined CDW state below 59 K [3.42]. This evidence is disputed by synchrotron X-ray measurements that confirm the localized picture painted above [3.43].

The localization of the two CDW's bears directly on the interpretation of the resistivity measurements that characterize the CDW transitions. Such measurements made on the Dalhousie samples are shown in figure 3.8. The CDW phase transitions are marked by two large resistance anomalies at 144.9 K and 59.0 K. It is important to remark that the transition to the Peierls state does
Figure 3.8 Resistance of NbSe$_3$ as a function of temperature.
not lead to the formation of a Peierls insulator as it did in o-TaS$_3$. On the contrary, NbSe$_3$ remains metallic over this entire temperature range. The conventional interpretation of these resistivity results (which agree with those previously reported [3.44]) maintains that the two separate phase transitions correspond to two strongly localized CDW on two of the three chain pairs. The third chain pair, Nb(II), does not participate in the CDW state and ensures a metallic channel for conduction over this range. This is reflected in an overall decrease in the sample resistance. The rise in the resistivity is due to the gapping loss of Fermi surface estimated from conductivity measurements to be 20% at 144 K and 80% of the balance at 59 K [3.45]. Thermoelectric power experiments identify the destruction of hole-like Fermi surface at the upper transition and electron-like Fermi surface at 59 K [3.46]. Hall effect [3.47] and magnetoresistance [3.48] measurements are also consistent with the development of a gap in the single-particle excitation spectrum. The specific heat has been measured for this compound and anomalies are noted at 144 K and 59 K [3.49]. Calculations based on these results estimate that 25% of free electrons condense into the CDW state at 144 K and a further 30% condense at 59 K.

The CDW order parameter has been deduced from X-ray scattering experiments and these show the smooth rise that is associated with second order phase transitions [3.50]. However, calorimetry does present evidence for a small latent heat at both transitions which would argue more properly for a first order transition [3.51]. It is suggested that the role of fluctuations in this
system has been neglected and that its proper treatment may resolve these apparent contradictions. The evidence for fluctuations comes from diffuse scattering above the phase transition [3.52] and also from the thermal expansion results found in the work presented here.

The 144 K CDW transition is also exhibited as a dip in the longitudinal Young’s modulus measured by the vibrating-reed technique [3.53]. However, no such anomaly is detected to within 2 parts in 1000 at the 59 K transition.

NbSe₃ also displays the dramatic non-linear resistive behaviour that is associated with the ‘sliding’ CDW state. An experiment is shown in figure 3.9 which illustrates this effect. Shown is the differential resistance plotted against the applied electric field for a sample taken from those grown at Dalhousie. This result is in all respects similar to the o-TaS₃ example save that the threshold field is more in keeping with samples of typical impurity concentrations (10¹⁸/cm³). This experiment along with the temperature variation of the threshold field pictured in figure 3.10 is in agreement with the results of previously published experiments [3.54]. Again, the theoretical descriptions mooted in the o-TaS₃ section find applicability here [3.23, 3.24, 3.25, 3.26].

The elastic properties are no less affected by the onset of non-linear conductivity. The longitudinal Young’s modulus experiences a dramatic softening when the electric field crosses threshold [3.55]. There are also broad-band noise observations [3.56] and narrow-band noise in the power spectrum of the CDW current [3.57]. The latter does not in fact follow equation 3 unless the wavelength
of the CDW is replaced by a figure 3.8 times as large [3.58]. The reason for this is not understood.

3.3 2H-TaSe$_2$

The 2H polytype of TaSe$_2$ was prepared at Dalhousie by the hVT technique combined with annealing above 600 C [3.59]. The source elements were 99.9999% pure tantalum and 99.9999% pure Selenium and Iodine was used as the transport vapour for the crystal growth which was completed in 2-3 weeks. The single crystals yielded by this technique were large, flat layered platlets between 0.5 and 1 mm thick and 1 mm$^2$ to 1 cm$^2$ in area. The surface of the crystals appeared dark and metallic. Under microscopic examination hexagonal patterns formed by screw dislocations served to identify the overall symmetry and orientation of the basal plane. This compound was soft and easily cleaved in the basal plane.

2H-TaSe$_2$ is a member of the transition-metal dichalcogenide (TMD) class which is characterized by layered structures. The fundamental structural unit is a layer of close-packed transition metal atoms sandwiched between two layers of close-packed chalcogen atoms (figure 3.11). The bulk crystal is made up of vast numbers of these sandwiches stacked one upon the other and bonded together by weak van der Waals forces [3.60]. Because of the various possible coordinations of the transition metal atoms within the sandwich and the possible stacking
Figure 3.9 Threshold electric field of NbSe$_3$ at 110 K.
Figure 3.10 Variation of threshold electric field of NbSe₃ with temperature.
sequences of the sandwiches there are a wide range of crystal polytypes [3.61].

Attention here is restricted to the 2H(a) polytype belonging to the space group P6₃/mmc. This crystal structure is distinguished by a two-layer unit cell, trigonal prismatic coordination of the chalcogens and overall hexagonal symmetry in the basal plane (figure 3.12). The material synthesized at Dalhousie and used in the experiments described herein was analyzed by powder X-ray diffraction which confirmed the 2H(a) structure [3.62]. The unit cell parameters for this compound were measured as \( a = 0.343 \text{ nm} \) and \( c = 1.271 \text{ nm} \), in agreement with earlier investigations [3.61].

The layer structure in tandem with the weak van der Waals bonding between layers suggests that this material is of reduced effective dimensionality. The typical conductivity anisotropy for materials of this class is about 30 [3.63]. A more direct probe is found in the Fermi surface measurements elicited from de Haas-van Alphen quantum oscillations [3.64]. These portray a quasi-two-dimensional band structure consisting of large cylinders of Fermi surface with axes parallel to the crystallographic c axis.

With an effective dimensionality of two the electron-phonon interactions are essentially confined to the basal plane. Under these conditions a transition to a Peierls state is considered quite likely. For 2H-TaSe₂ such a transition occurs at approximately 122 K and is associated with a large resistivity anomaly reminiscent of the CDW transitions in NbSe₃. The data in figure 3.13 shows the presence of this anomaly at 121.8 K for the material grown at Dalhousie.
Figure 3.11 Hexagonal close-packed layers of the TMD compounds (after reference 3.60)
Figure 3.12 Co-ordination of 2H-TaSe$_2$ (after reference 3.60)
The character of the CDW state in 2H-TaSe$_2$ is worth exploring in detail because of its complex domain structure. The CDW lies completely in the basal plane of the crystal and reflects the hexagonal symmetry of the host lattice. Data drawn from X-ray diffraction [3.65] and neutron diffraction [3.66] experiments reveal that the CDW is characterized by a triplet state which is incommensurate immediately below the 122 K phase transition. Since there are three equivalent directions in the hexagonal basal plane three CDW's form, each at an angle of 120° to each other. The wavevector of these CDW's follows $q = a^*(1-d)/3$ where $d$ is a measure of the incommensurability of the CDW's. When $d = 0$ each would lie in registry with the lattice with a commensurability parameter of 3.

In addition to the complication of the triplet CDW state there is the existence of discontinuities in local phase of the incommensurate CDW termed discommensurations (DC). These have already been mentioned in connection with α-TaS$_3$. The drive to take advantage of the commensurability energy forces the incommensurate CDW's to form lattices of DC's. The existence of these DC's has been confirmed by NMR measurements [3.67]. The combination of DC's and a triplet CDW state yields the complex phase structure that follows.

When 2H-TaSe$_2$ is cooled below 122 K it undergoes a phase transition into a triplet incommensurate CDW state. It is thought that this transition is predominantly second order with a weak first order component [3.68]. Further evidence for this comes from an observed discontinuity in the dilation as well as in its temperature derivative, the thermal expansion coefficient [3.69, 3.70]. However,
Figure 3.13 Resistance of 2H-TaSe$_2$ as a function of temperature.
Helium atom surface scattering measurements firmly identify the transition as second order [3.71]. The high resolution thermal expansion results reported in this work taken with specific heat measurements [3.72] support the purely second order character of this transition.

The triplet ICDW state immediately below 122 K contains DC's which organize themselves into a double honeycomb pattern with hexagonal symmetry, the so-called 'hex'phase. Further cooling sees the DC density decrease gradually as the CDW heads for a commensurate state in all three directions. This state is achieved in a continuous transition at 84 K as all three CDW's become commensurate with a commensurability parameter of 3. The symmetry of this state is orthorhombic rather than hexagonal as was previously thought [3.73].

If this material is now warmed from below 84 K the triplet CCDW state persists until 93 K where two of the three CDW's become incommensurate while the third remains commensurate. The interaction of the DC lattice in the two ICDW's yields a simple 'stripe' phase with the stripes of DC's oriented perpendicular to the CCDW wavevector. The choice of direction for the CCDW is random and no doubt influenced by defects and impurities. This random orientation leads to the formation of domains of striped regions [3.74]. A single orientation of the striped phase domains can be attained by the application of uniaxial or shear stress in the basal plane [3.75].

By warming beyond 112 K the transition from stripe to hex phase is accomplished as the third CCDW becomes incommensurate. The final stage is a
transition to the normal state above 122 K.

The CDW transition at 122 K is marked by the resistivity effects noted above and in other work [3.76]. In addition, specific heat measurements note the presence of an anomaly at this temperature [3.72]. Elasticity experiments using the vibrating-reed [3.77] and ultrasonic velocity [3.69] techniques show a small anomaly in the basal plane compliance at 122 K and a very large one near 93 K. The coefficient of thermal expansion reveals discontinuities in the dilation and in the temperature derivative of this dilation near the normal/ICDW transition at 122K, the Commensurate/Incommensurate transition at 93 K and at the stripe/hex transition at 112 K [3.69, 3.70].

2H-TaSe$_2$ differs in an important way from the chain compounds considered earlier in that the CDW is two-dimensional in character. For this reason no non-linear threshold effects have been observed in its transport properties [3.78].
Chapter Four  Test of System by Application to 2H-TaSe$_2$

One of the principle goals of the design of the dilatometer is the study of structural changes associated with the phase transitions in quasi-one-dimensional CDW compounds. Dilation measurements are ordinarily inaccessible in these materials with any great resolution or accuracy. In order to gauge the sensitivity of the probe the Normal to ICDW phase transition in 2H-TaSe$_2$ is examined in detail. Although not a quasi-one-dimensional material, 2H-TaSe$_2$ can be cut and cleaved to simulate as far as possible the mechanical properties of such materials. Moreover, this compound is well characterized and its phase transitions extensively studied by other techniques [4.1, 4.2, 4.3].

4.1 Description of Experiments

The 2H-TaSe$_2$ was removed from the quartz growth tube and cleaved parallel to the basal plane until between 200 and 300 microns thick. Thin (ca. 300 micron) strips were cut parallel to the hexagonal screw dislocation observed on the surface of the crystal using a sharp razor blade. All samples had their dilation measured parallel to the reciprocal lattice vector $a^*$ in the basal plane. The typical length of samples varied from 1 to 3 mm. Fine gold wires (25 micron
diameter) were attached to the ends of the samples in a four-point resistance configuration. The resistance was monitored by a continuous AC phase-locked-loop technique as discussed in chapter two.

Another purpose of these experiments was the determination of the optimum parameters for the construction and application of the cantilevers used in this configuration. Three were tried: a small crystal of carefully cleaved NbSe$_2$, a composite lever fashioned from a .004" o.d. Molybdenum wire loop with an HOPG surface attached, and a .005" thick phosphor-bronze strip also with an HOPG surface attached. The NbSe$_2$ put the least uniaxial strain on the samples (roughly 0.00041 MPa) and provided a ready surface for tunnelling in situ but was difficult to prepare. The Molybdenum wire levers were simple to construct and placed a uniaxial stress of about 0.59 MPa on the samples. These two levers suffered, however, from an insufficient resistance to torque applied by the tunnelling tip. The conditions under which these experiments were carried out were not UHV. Consequently, a contamination layer was present between the tip and the surface requiring a certain force to bring the tip to within tunnelling distance [4.4]. If there was misalignment between the principle axis of the lever and the tip a torque built up which tended to destabilize the system. The phosphor-bronze lever was constructed to resist this torque at the cost, however, of a greatly increased uniaxial stain applied to the sample, on the order of 8.9 MPa. The best results for the 122 K transition were obtained from the phosphor-bronze lever but it is well to recall the stress present when reviewing the phase
structure at lower temperatures.

After the sample was mounted in the dilatometer the sample space was evacuated to 100 microns and helium exchange gas bled in to about 0.5 atmospheres to speed temperature equilibration between sample and probe. The probe was typically cooled to liquid nitrogen temperatures and allowed to warm slowly at about 4.5 K/hr. Previous experiments operating the probe purely as a conventional dilatometer established that such a warming rate was sufficient to dismiss temperature gradients in the system. In several experiments the dilation was monitored while the probe was freely cooling. The probe temperature was expected to lag the sample in this case.

4.2 Results at 122 K

High resolution dilation measurements were made over a 15 K range centred over the N/ICDW phase transition in 2H-TaSe$_2$ at 122 K. The resolution of the temperature measurement was 0.02 K but averaging increased this to 0.05 K for the purposes of a numerical derivative. The dilation resolution varied with the tip-to-surface conditions but in the best and most reproducible results was better than 5 parts in $10^7$. The results shown in figure 4.1 include the best series of data taken with a phosphor-bronze lever. The curves are off-set for clarity. These results all show a transition temperature at 121.8 K but it is not unusual to encounter a variation of 0.5 K in this figure from samples of different growth lots.
Figure 4.1 Raw dilation results for 2H-TaSe$_2$ near the N/ICDW phase transition.

Curves off-set for clarity.
However, the shape of the dilation was generally unaffected by these differences.
The logarithmic derivative of the 122 K phase transition with respect to temperature has been determined to be 0.0284 GPa\(^{-1}\) [4.5]. This hydrostatic pressure measurement allows a crude estimation of the upper limit of the depression of the transition temperature due to uniaxial stress. For the largest stress imposed on the samples the shift in the transition temperature was never more than 0.015 K, well below the resolution of the experiment.

The results used in the analysis below were obtained from a sample of 2H-TaSe\(_2\) 2.63 mm long, 0.33 mm wide and 0.07 mm thick. The lever used was a .005" thick phosphor-bronze strip 4.46 mm long and 2.24 mm wide. The mechanical bias applied at room temperature was 0.16 mm resulting in a room-temperature uniaxial stress of 8.9 MPa. The change in this value due to relative expansions of the sample and gallows was estimated to be less than 5 percent.

These three raw dilation curves were taken from two separate rough approaches, indicating that the HOPG surface did not influence the results unduly. This was because the use of the rough-approach mechanism undoubtedly resulted in a lateral shift in the tip position over the HOPG surface. The average thermal expansion coefficient over this range has been measured by X-ray dilatometry at 3.3 ppm/K [4.6]. The only claim made here is that the background expansion is constant so that the raw data slope has been adjusted accordingly.
4.3 Analysis near the N/ICDW phase transition

The analysis of the normal-to-incommensurate CDW (N/ICDW) phase transition at 122 K will address three topics. These are the specific order of the phase transition, the results of an Ehrenfest analysis including Testardi’s extension below $T_C$ and finally the role of fluctuations about the critical temperature.

4.3.1 Order of the N/ICDW transition

The N/ICDW phase transition at 122 K has been examined extensively from both a theoretical and experimental point of view. However, the precise order of this transition remains ambiguous. The present theoretical description of the incommensurate CDW state as a network of discommensurations allows two possible models. The first reveals a honey-comb network of discommensurations that fails to break the hexagonal symmetry of the triplet CDW state. The order parameter must include six components and the model predicts a first order N/ICDW phase transition [4.7]. The second model assembles the discommensurations in a network of parallel lines that lowers the symmetry in the basal plane to orthorhombic. The phase transition associated with this model is exclusively second order [4.8]. Thus the theoretical treatments support either phase transition.

From an experimental point of view the evidence for a first order component in the N/ICDW phase transition remains rather weak. It is possible to interpret the
two thermal expansion measurements available as evidence of a first-order component in the CDW phase transition in this system [4.1, 4.2].

On the other hand there is much experimental evidence that points to an exclusively second order phase transition at 122 K. The measured anomaly in the Young' modulus associated with the N/ICDW transition shows no hysteresis to within the experimental uncertainty of the procedure [4.9]. As well, the specific heat measurements of J.M.E. Harper et al. [4.10] show no evidence of hysteresis. The absence of hysteresis (and the latent heat it implies) typically rules out a first order phase transition. Craven and Meyer [4.11] have made a detailed examination of the specific heat about the CDW phase transition using an AC calorimeter. These authors eschew any first order component to the phase transition and describe their results within the framework of a fluctuation model. Brusdeylins et al. [4.12] have applied helium atom surface scattering to the study of the temperature evolution of the CDW corrugations on the surface of 2H-TaSe$_2$. These experiments are also cast in a fluctuation model and no evidence for a first order N/ICDW phase transition is detected.

The dilation results presented in this chapter support an exclusively second order phase transition at 122 K. In figure 4.2 the linear "background" dilation (which would include elements of both the cell and sample dilation) is removed from the dilation signal in order to show the transition region in more detail. The strong curvature in the dilation signal below the transition shows no evidence of a discontinuity in the dilation to within an accuracy of 0.5 ppm and a resolution of
Figure 4.2 Dilation of 2H-TaSe$_2$ with a linear background subtracted in order to emphasize detail.
0.02 K. These results are, moreover, reproducible from sample to sample and run to run. Consequently, the N/ICDW phase transition at 122 K is taken to be exclusively second order in character.

4.3.2 Mean Field Analysis at the N/ICDW phase transition

With the conclusion that the N/ICDW transition is purely second order in character it is possible to analyze the results with Ehrenfest’s relations. In these experiments all directional components are confined to the basal plane of 2H-TaSe₂. The dependence of the transition temperature on uniaxial stress applied in the basal plane is not known. Only the isotropic pressure derivative has been measured [4.5]. The specific heat [4.11] and elastic modulus in the basal plane [4.9] are available in the vicinity of the phase transition. The elastic modulus does contain an anomaly near the phase transition at 122 K but its interpretation is difficult. Reasonably general thermodynamic arguments predict that the specific heat and the elastic modulus are connected by a scaling factor equivalent to the logarithmic derivative, \(- T_c(d \ln T_c/d \eta_i)^2\) [4.9]. The specific heat at the phase transition may be seen to rise as shown in figure 4.3 drawn from Craven and Meyer [4.11]. This would typically lead to a falling elastic modulus in the same interval but in fact the modulus rises sharply [4.9]. The reason for this is unknown. As a result the Ehrenfest analysis is restricted to comparisons of the specific heat and the coefficient of thermal expansion.

The coefficient of thermal expansion of 2H-TaSe₂ was obtained numerically from
the raw data shown in figure 4.1. The technique used was that of a linear least-squares fit (LSF) using anywhere from 3 to 9 adjacent points. The slope calculated was then attributed to the centre point of the set used. It was found that 7 points was sufficient to calculate the derivative with a reasonable noise level without appreciable 'smearing' of the data. For the resolution of these measurements this is equivalent to a 0.35 K "window". The Lagrangian method was briefly considered as an alternative but the formulation for more than 5 points was much more complex and the results were not superior to those of the LSF. The results of the application of the LSF method with 7 points is shown in figure 4.4. Again, these curves are off-set for clarity; the lowest curve is correctly scaled. The oscillations are not artifacts of the derivative technique but it is felt that they are not associated with the sample per se. Rather, the size of the oscillations (ca. 0.2 nm) is consistent with undulations in the HOPG surface inevitably 'scanned' as the surface and tip expand relative to each other. These two results were then averaged into the single curve shown in figure 4.5. By means of an extrapolation above and below the transition the mean-field step in the thermal expansion coefficient may be estimated for this transition. The value extracted is + 2.6 (+/- 0.1) ppm/K.

In figure 4.3 the specific heat results of Craven and Meyer are shown together with the mean-field step that these authors estimate for the transition at 122 K. The step is approximately 5.8 (+/- 0.1) J/mole-K. The estimate of the transition temperature's dependence on uniaxial stress applied in the basal plane yields the
Figure 4.3 Specific heat of 2H-TaSe$_2$ at constant pressure near the N/ICDW transition. Broken line shows the estimated mean-field step. (after reference 4.11).
value of -0.0170 (+/- 0.0006) GPa$^{-1}$. This value is comparable in magnitude to the pressure dependence of the same transition, +0.029 (+/- 0.002) GPa$^{-1}$ as estimated by Chu et al. [4.5] or +0.020 (+/- 0.002) GPa$^{-1}$ as estimated by Feldman et al. [4.6]. The sign indicates that the transition is depressed by the application of uniaxial stress in the CDW plane, a result which is generally consistent with measurements on related CDW systems [4.13]. Criticisms may be levelled against the extrapolation of discontinuities in the specific heat and thermal expansion shown in figures 4.3 and 4.5 respectively. Never-the-less, the specific heat and thermal expansion data clearly share similar features which suggest a close thermodynamic relationship. Bearing this in mind a different tack may be taken with this data. An extension of the Ehrenfest relations to temperatures below $T_c$ may be employed after a scheme first laid out by L.R. Testardi [4.14].

Within Testardi's approach the difference per unit mole between the Gibbs free energy of the transformed and un-transformed phases is given the general form (simplified for a single-component system),

$$
\Delta G = \xi(\eta) \int \left[ \frac{T}{T_c(\eta)} \right]
$$

(1)

where the order parameter amplitude, $\xi$, and the transition temperature $T_c$ are both functions of the stress, $\eta$. This formulation has been used with some success in ferroelectric, ferromagnetic and superconducting systems. The latter is of particular interest here since the microscopic theories of superconductivity and CDW's have a great deal in common [4.15]. The definition of the 'excess' of any
Figure 4.4 Coefficient of thermal expansion of $2\text{H-TaSe}_2$ near the N/ICDW phase transition. The upper curve has been offset by 5 ppm/K for the sake of clarity.
Figure 4.5 Coefficient of thermal expansion of 2H-TaSe$_2$ obtained by averaging the curves in figure 4.4. Solid line shows the estimated mean-field step for the transition.
property, \( X \), of the system under transformation is,

\[ \Delta X = X^H(T) - X^L(T) \quad (2) \]

for all \( T < T_c \). Here \( X^H(T) \) is the observed high-temperature behaviour of the system extrapolated to temperatures below \( T_c \). \( X^L(T) \) is the actual behaviour of the system below \( T_c \).

Testardi's analysis, general though it is, leads to an intimate connexion between the 'excess' specific heat and the 'excess' thermal expansion in terms of the stress derivatives of the order parameter amplitude and the transition temperature,

\[
\Delta \alpha_j = - \left( \frac{d \ln T_c}{d \eta_j} \right) \Delta C_p(T) \\
+ \left( \frac{d \ln \xi}{d \eta_j} - \frac{d \ln T_c}{d \eta_j} \right) \int_T^{T_c} \frac{\Delta C_p(T')}{T'} dT'
\]

(3)

where \( j \) is the direction of the expansion measurement. Note that the Ehrenfest relation is recovered at \( T = T_c \). This expression roughly predicts that the excess thermal expansion and the excess specific heat will resemble each other through the scaling factor, \( -d \ln T_c/d \eta_j \).

In order to begin this analysis the "excess" quantities of thermal expansion and specific heat must be calculated. In the case of the thermal expansion the high temperature behaviour was fitted to a straight line between 124 and 130 K. This line was then extended below \( T_c \) (= 121.5 K) and the excess thermal expansion
Figure 4.6 "Excess" thermal expansion near the N/ICDW transition in 2H-TaSe$_2$. 
calculated as shown in figure 4.6.

The specific heat was estimated from published data gathered from a different sample [4.11]. High resolution data between 117 and 124 K allowed the estimation of the specific heat to within 1%. Coarser data over the range of 90 to 160 K permitted the calculation of the high temperature linear behaviour. The calculation of the excess entropy (the final term in equation 3) was made by means of a numerical integration of the excess specific heat from the transition temperature with an intrinsic error of less than 10%. It must be noted however, that in order to bring the transition temperatures of the thermal expansion and the specific heat into agreement the latter must have its temperature scale shifted by 0.88 K. This rather dramatic manipulation of the data is perhaps justified by the oft-mentioned sample dependence associated with these materials [4.2, 4.11]. The excess specific heat (after temperature scale shift) is shown together with the excess thermal expansion in figure 4.7.

The two curves in figure 4.7 tend to confirm the assertion by Testardi that the excess specific heat and the excess thermal expansion will resemble each other. The scale factor provides a rough estimate of the logarithmic derivative of the transition temperature with respect to uniaxial stress in the basal plane; in this case it is \(-0.013 \text{ GPa}^{-1}\), not too different from the figure of \(-0.015 \text{ GPa}^{-1}\) calculated from the estimated mean field steps. This figure does not include the effect of the excess entropy which is fully accounted for in the analysis below.

A more refined estimate of both the logarithmic derivative of the transition
Figure 4.7 "Excess" specific heat and "excess" thermal expansion for 2H-TaSe$_2$. 
temperature and the order parameter with respect to uniaxial stress in the basal plane may be made as follows. The excess thermal expansion and the excess entropy are both divided by the excess specific heat at particular temperatures below $T_C$. These are plotted against each other and fitted to a straight line. The intercept of this line is the logarithmic derivative of the transition temperature with respect to uniaxial basal plane stress. The slope is the difference between this latter quantity and the logarithmic derivative of the order parameter amplitude with respect to uniaxial basal plane stress. This 'Testardi' plot is illustrated in figure 4.8. The quantities obtained in this manner are,

$$\frac{d\ln T_C}{d\eta_a} = -0.015 \ \text{GPa}^{-1}$$

$$\frac{d\ln \xi}{d\eta_a} = +0.256 \ \text{GPa}^{-1}$$

each to a precision of 10 percent.

It will be noted that the determination of the basal plane stress dependence of the transition temperature is relatively insensitive to the mean-field technique used to arrive at its value. The mean field "step" at $T_C$ yields a stress dependence of $-0.016 \ \text{GPa}^{-1}$ while the full Testardi treatment modifies this to $-0.015 \ \text{GPa}^{-1}$. These values are in accordance with previous estimates based on the elastic moduli results of Barmatz [4.9]. In order to estimate the c-axis stress dependence a reliable value of the pressure dependence of this phase transition must be found. The value deduced by Chu et al. from their resistivity measurements near $T_C$ is $+0.029 \ \text{GPa}^{-1}$ [4.5]. This value is criticised by Feldman et al. [4.6] as being too
Figure 4.8 "Testardi" plot for 2H-TaSe$_2$ below the N/ICDW phase transition.
large based on the data quoted for $T_c$ vs $p$. By taking a linear fit to the data below 0.5 GPa these authors calculate the smaller value of 0.020 GPa$^{-1}$ for $d\ln T_c/dp$. This reduces the Chu et al. figure by roughly 30%. In either case the c-axis stress dependence for a system with hexagonal symmetry may be calculated from,

$$\frac{d\ln T_c}{d\eta_c} = -\frac{d\ln T_c}{dp} - 2 \frac{d\ln T_c}{d\eta_a}$$  \hfill (4)

Taking the value of Chu et al. the stress dependence of $T_c$ in the c-axis direction is +0.005 GPa$^{-1}$. The Feldman et al. value increases this figure to +0.016 GPa$^{-1}$. Both these figures are comparable in magnitude to the basal plane stress dependence of approximately -0.020 GPa$^{-1}$ and cannot be called negligible.

4.3.3 Fluctuations at the N/ICDW phase transition

The above analysis was based on a mean-field approach which completely ignores the contribution of fluctuations in the vicinity of the N/ICDW phase transition. There is strong evidence that fluctuations exist in this system. The analysis of Craven and Meyer [4.11] shows that a power-law dependence on reduced temperature may be expected in the specific heat up to 6 K on either side of the transition temperature. These same authors also find that the resistivity exhibits a similar power-law dependence in the region of the phase transition. To these results may be added the He atom surface scattering data of Brusdeylins et al. which displays a power-law relationship in the excess surface
corrugations associated with the CDW in 2H-TaSe$_2$ [4.12].

Craven and Meyer use their specific heat data derived from AC calorimetry in a range of roughly 7 K about $T_c$. The authors assume a linear background specific heat which is the contribution of the lattice. Accordingly, they fit their data to the power law,

$$C_p^+ = \frac{A^+ (t^{-\alpha} - 1)}{\alpha} + B^+ + D t$$

for $T > T_c$ and,

$$C_p^- = \frac{A^- (|t|^{-\alpha'} - 1)}{\alpha'} + B^- + D t$$

for $T < T_c$ where $t$ is the reduced temperature, $T - T_c / T_c$ and $D t$ is the lattice background.

Craven and Meyer are able to show that their data supports equivalent exponents on either side of the transition and so are able to merge all their specific heat data into one set. This merged set is then fitted to the equations above by a least-squares technique. The global minimum for their data gives a critical exponent of $\alpha = 0.45 (+/-0.035)$ with the coefficients $A = 0.191 (+/-0.036)$ and $B = 14.1 (+/-0.2)$. This value of the critical exponent is very large when compared to theories of asymptotic universality. However, if the transition is described by Gaussian fluctuations, the lowest-order extension of mean field theory, then the specific heat would diverge like $t^{2-d/2}$. For a system with 3-
dimensional fluctuations \( d = 3 \) and the critical exponent would be 0.5 [4.16]. It is suggested that this nearly mean field behaviour is the result of the system being near a tricritical point. A theoretical model based on amplitude and phase variations in the ICDW state would support this assertion [4.17].

The Helium atom surface scattering results present a similar picture [4.12]. Here, the authors use a monochromatic beam of helium atoms to measure the excess surface corrugation of the CDW about the phase transition. Their best fit to the data yields a critical exponent of \( 1/3 \). However, the uncertainty is large enough to admit a critical exponent of \( 1/2 \). The figure of \( 1/3 \) might correspond to a 3D-XY model of the N/ICDW transition [4.18]. A value of \( 1/2 \) would be appropriate to the lowest order extension of mean field theory.

The strong curvature in the dilation signal below \( T_c \) and the weak curvature above suggest that this data might lend itself to a similar analysis [figure 4.2]. It is usual in these deliberations to assume that the specific heat and coefficient of thermal expansion share the same critical behaviour [4.19]. Accordingly, the thermal expansion is presumed to follow,

\[
\gamma = \frac{A(t^{-\alpha} - 1)}{\alpha} + B + Dt \quad (7)
\]

where \( \gamma \) is the thermal expansion and \( D \) is the linear background. In the temperature range from 116 K to 126 K there is little change in the background [4.6]. This may be seen in the graph of the expansion in figure 4.4. \( D \) is thus set to zero.
Using the numerically-derived thermal expansion in a fitting procedure is not the best route in this instance. Rather, the thermal expansion in equation 7 is integrated to extract the dilation signal expected from this power-law model,

\[
\frac{\Delta L}{L} = T_c \int_{T_1}^{T} \gamma(t') dt'
\]

whence,

\[
\frac{\Delta L}{L} = \frac{T_c A}{\alpha (1 - \alpha)} t^{1-\alpha} + T_c (B + \frac{A}{\alpha}) t + C
\]

This function was fitted to the dilation data above and below the phase transition in a reduced temperature range from \( t = 0.05 \) to \( t = 0.0008 \). Various exponents were examined between 0.1 and 0.9 while the background C was held constant above and below \( T_c \). The result for a critical exponent of 0.5 is shown in figure 4.9.

Owing to the noise in the dilation data it is not possible to make an unambiguous determination of the critical exponent for this system. Such determinations are notoriously difficult with the best resolved data and great care must be exercised in the fitting routines. Here, over the exponent range from 0.1 to 0.9 a fit was always possible with an r value ("goodness-of-fit") above 0.96. Consequently, all that may be concluded from the dilation data is that it is consistent with either exponent of 1/2 or 1/3.
4.4 Results at 112 K

The phase transition at 112 K is a first order transition present only on warming out of the stripe phase into the hexagonal phase. There is a strong hysteresis associated with the stripe phase owing to the formation of domains in which only one of three possible \( q \)-vector directions is favoured. It should be pointed out that there is evidence for the orientation of these domains by the application of uniaxial and shear stresses in the basal plane [4.20, 4.21]. It is with this in mind that the results of dilation experiments with varying stresses are approached. Figure 4.10 shows the data taken from 2H-TaSe\(_2\) for three different uniaxial stresses, each offset for clarity. Note that for each of the stresses labeled the data is reproducible. It is believed that the top curve represents the first measurement of the dilation associated with the stripe/hex phase transition for nearly zero uniaxial stress. The size of the anomaly is -16.6 ppm which is much larger than previously measured for this material. The only difference is that the previous measurements almost certainly employed conventional dilatometers which must bring to bear some uniaxial compression in order to operate properly. The middle curve shows an anomaly of -5.1 ppm while the bottom curve has this reduced to -2.3 ppm. The three curves may be scaled into each other almost perfectly. These results may not be at odds with those of previous experiments if the variations in the stress are taken into account and their effects on domain alignment in the stripe
Figure 4.9 Dilation of 2H-TaSe$_2$ with linear background expansion removed. Solid lines are a least-squares fit corresponding to a critical exponent of 0.5.
Figure 4.10 Raw dilation of 2H-TaSe$_2$ near the stripe/hex phase transition. Data is off-set for clarity. Labels correspond to uniaxial stress in the basal plane:

\[ a = 8.9 \text{ MPa}, \quad b = 0.59 \text{ MPa}, \quad \text{and} \quad c = 0.00041 \text{ MPa}. \]
phase examined. The dilatometer of Simpson et al. [4.2] measured this anomaly at -4.4 ppm while the instrument of Steinitz and Grunzweig-Genossar [4.1] showed -1.5 ppm. It remains to establish the size of the uniaxial stresses involved. This experiment points out the care that must be taken when operating the dilatometer in the cantilever mode on samples with domain or other stress-dependent factors involved. On the other hand, the cantilever mode is in many ways ideally suited to a systematic study of these effects allowing the straight-forward application of both shear and uniaxial stresses in the basal plane.

4.5 Results at 93 K

The first order transition at 93 K is a result of the transition from the triply commensurate CDW state to a stripe phase with its attendant domain formation. Again, these have been measured previously but with wide variations among different experimental groups [4.1, 4.2]. The results for the tunnelling dilatometer are no different (figure 4.11). For a light uniaxial loading of 0.00041 MPa the C/I transition is -29.3 ppm in size and is 3.7 K wide. When the loading is increased to 8.9 MPa the size of the anomaly almost doubles to -53.3 ppm but the width of the transition increases to 16 K and the transition temperature is increased by 2.5 K. However, these results were not repeated and as such must be viewed with caution. They are shown here in order to complete the picture of the phase structure in this material. What seems clear is that great care must be exercised when loading such samples with strong levers.
Figure 4.11 Raw dilation of $2\text{H-TaSe}_2$ near the C/I transition. Labels correspond to uniaxial stress in the basal plane: $a = 8.9$ MPa, $b = 0.00041$ MPa. $T_C$ is nominally 93 K for zero uniaxial stress [4.2].
4.6 Conclusion

The experiments described here were originally undertaken with a view to evaluating the technique of tunnelling dilatometry. The results obtained using $2\text{H}\text{-TaSe}_2$ as a test sample confirm the validity and accuracy of this technique and the apparatus that supports it.

As an unexpected dividend high accuracy, high resolution dilation results were obtained in the region of its N/ICDW phase transition at 122 K. To these may be added data in the vicinity of the stripe/hex phase transition at 112 K and the C/I transition at 93 K.

The N/ICDW transition results are of sufficient accuracy to allow an extensive analysis based on both mean field and fluctuation models. It may be concluded in the first place that the N/ICDW is exclusively second order with no first order component at all. This is based on the absence of any dilational discontinuity near the 122 K phase transition in this material.

An exclusively second order phase transition at 122 K has two important consequences. In the first place, the second order phase transition argues for a non-negligible inter-layer interaction in the CDW state. This result is a consequence of the Landau theory of this transition developed by McMillan [4.22]. The existence of a Coulomb interaction between layers of $2\text{H}\text{-TaSe}_2$ in the CDW state is supported by the neutron-scattering data of Moncton [4.23] which shows that the CDW's in adjacent layers will adjust their phasing in order to minimize
their electrostatic energy.

The second important implication of the second order phase transition is found in the symmetry of the ICDW state immediately below $T_C$. A second order phase transition will support a discommensuration lattice with an orthorhombic symmetry in contrast to the hexagonal symmetry of the proposed honey-comb arrangement. The orthorhombic symmetry is observed in both neutron-scattering experiments [4.23] and in dark-field electron microscope images [4.24].

The N/ICDW phase transition near 122 K has been analyzed in a mean field treatment by Ehrenfest's relations at $T_C$ and by Testardi's extension to temperatures below $T_C$. The results obtained for the basal plane stress dependence of the transition temperature are relatively insensitive to the method used to calculate this figure which is approximately -0.017 GPa$^{-1}$. The sign of this quantity is consistent with observations on related CDW systems while the magnitude is comparable to the pressure dependence of the same transition. A corresponding estimate of the c-axis stress dependence of the N/ICDW transition yields a value of either +0.005 GPa$^{-1}$ or +0.016 GPa$^{-1}$ depending on the figure used for the pressure dependence. The values so derived are comparable to the basal plane stress dependence of $T_C$ and thus the interlayer interaction cannot be considered to be negligible. The sign of the c-axis stress dependence suggests that intercalation in 2H-TaSe$_2$ would raise the N/ICDW transition temperature although this ignores the possible impurity effects associated with such a system.

It would appear that the interlayer interactions may not be overlooked in
comparison with the basal plane interactions when considering the formation and stabilization of the ICDW state immediately below $T_c$. An unusually large value for the Young's modulus in the basal plane has been measured by Barmatz et al. [4.9] who argue that this is indicative of a strong elastic coupling between the layers of this material. The Landau treatment of McMillan [4.22] also suggests that a non-negligible interlayer interaction is necessary for the N/ICDW transition to be exclusively second order.

Using the basal plane stress and pressure dependence of the N/ICDW transition together with the elastic constants the effective "two-dimensionality" of 2H-TaSe$_2$ may be estimated. This anisotropy figure is calculated from the ratio of the stress dependence of the transition temperature in the c-axis to that in the basal plane,

$$ r = \frac{\left( \frac{dT_c}{d\varepsilon_i} \right)}{\left( \frac{dT_c}{d\varepsilon_j} \right)} $$  \hspace{1cm} (10)

When $r = 0$ the material is perfectly two-dimensional. For a hexagonal system the stress dependences depend on the strain dependences and the elastic constants,

$$ \frac{dT_c}{d\varepsilon_i} = \frac{dT_c}{d\sigma_a} (2c_{13} - 2c_{33}) - c_{33} \frac{dT_c}{dp} $$  \hspace{1cm} (11)
\[ \frac{dT_c}{de_1} = \frac{dT_c}{d\sigma_a} \left( 2c_{11} + c_{12} - 2c_{33} \right) - c_{13} \frac{dT_c}{dP} \]  

(12)

The elastic constants are extracted from the long-wavelength phonon dispersion data of Moncton et al. [4.28]; \( c_{11} = 23, c_{12} = 10.7, c_{33} = 5.4 \), all in units of \( 10^{11} \) dynes/cm\(^2\). The value of \( c_{13} \) is deduced from the elastic-moduli Debye temperature that is consistent with the Moncton et al. neutron scattering data and is \( 1.0 \times 10^{11} \) dynes/cm\(^2\) [4.6]. These lead to a value of \( r = -0.03 \) which suggests strong two-dimensionality in 2H-TaSe\(_2\) however, with non-negligible interlayer interactions.

The mean field deliberations above ignore the obvious existence of fluctuations in this system. Following the fluctuation treatment of Craven and Meyer the equation for the presumed thermal expansion coefficient is integrated to allow a fit to the raw dilation data. The least-squares fit to this data cannot pronounce on the critical exponent in this system: the results are consistent with any exponent between 0.1 and 0.9. If the exponent of Gaussian fluctuations is taken to be correct for this system then the mean field step deduced from the fitting parameters is 1.76 ppm/K. If the critical exponent of 1/3 is taken as correct then the mean field step in the thermal expansion is 2.5 ppm/K. These values are comparable to the mean field step deduced by extrapolation of 2.6 ppm/K and suggests a certain consistency among these various treatments.
Chapter Five  Active Dilatometry

5.1 Introduction

Under certain circumstances it is possible to exploit the internal Joule heating of fine-wire samples to make a determination of the absolute coefficient of thermal expansion. For such cases the sample acts as both the heat source and the thermometer for the measurement. Typically, the mass of the sample will be eight orders of magnitude smaller than the probe in which it resides. The use of small amounts of power makes it unlikely that the sample’s rise in temperature will in any way affect the temperature of the probe. Thus, dilation measurements can be made without the complication of a cell correction.

The technique may be briefly described. The sample is mounted in the cantilever mode which allows for the application of four-point resistivity contacts without disturbing the dilation measurement. The temperature of the sample is gradually raised by increasing the voltage across and consequently the Joule heating within the sample. Simultaneous measurements are made of the dilation, voltage, current and differential resistance of the sample. The temperature of the sample may be established with reference to the differential resistance or may be determined in a phenomenological manner from the quantity of dissipated power.
The use of either of these techniques is dictated by the specific circumstances of the experiment.

The temperature distribution within the sample is crucial to the proper interpretation of the "active" dilatometry experiments. Ideally, the entire sample should be at a single temperature throughout its length. In practice the anchor points of the cantilever mode mounting will require that the ends of the sample be at the same temperature as the probe body. The most that may be hoped for is a temperature distribution along the length of the sample that is nearly uniform over the entire length and which falls sharply to the probe temperature at the ends. In what follows this aspect of the active dilatometry technique is explored through a simple model. The aim of this model is to reproduce the essential features of the system while remaining mathematically tractable. For the purposes of this chapter order of magnitude estimates are deemed to be sufficient. Much of the justification for the active dilatometry technique can be argued ex post facto from the observations contained within the experiments themselves.

5.2 Simple Model of System

The construction of the simplified model of the experimental system has two purposes. In the first place, as described above, the temperature distribution within the sample must be ascertained to be reasonably uniform. In addition, the investigation of the modes of heat dissipation serves to guide the
phenomenological conversion of dissipated power into temperature.

In figure 5.1 the true disposition of the fine-wire sample with respect to the dilatometer cell is pictured. The sample is mounted in the cantilever mode which has the effect of thermally anchoring the sample’s ends to the probe. The mass of the probe is so large that it will be considered to be a reservoir of heat at temperature $T_w$. The sample lies near the centre of a roughly circular cavity of radius 0.45 cm. The sample is rectangular in cross-section with dimensions of no more than 10 microns by 10 microns and a length of 6 to 7 mm. It generates heat internally by means of the Joule effect which raises its temperature to $T_s$. The space between the probe and the sample is filled with helium exchange gas at approximately 30 kPa.

In figure 5.2 the complex arrangement above is reduced to its essential elements. The fine wire sample is given a cylindrical cross-section of radius 6 microns and a length of 6 mm. A cylindrical cross-section is employed to simplify the geometry. With an aspect ratio of between 500 and 1000 the details of the sample cross-section are expected to be unimportant to the overall behaviour. The sample now lies on the axis of a cylindrical cavity of radius 0.45 cm. The cavity wall remains at a fixed temperature, $T_w$, and the space between the sample and the wall is filled with helium exchange gas at 30 kPa. The ends of the sample are anchored to the cavity.

Two experiments are considered in this chapter, one on NbSe$_3$ and the other on $\alpha$-TaS$_3$. Both samples have approximately the same dimensions and are mounted
Figure 5.1 Cross-section of actual disposition of sample within experimental cell.
Figure 5.2 Diagram of the simple model of the sample within the experimental probe. Sample cross-section is greatly exaggerated.
in the same manner. They only differ in the extremes of power applied and the consequent temperature excursions. For NbSe$_3$, the dissipated power never exceeded 0.6 mW. Such a relatively small power resulted in a temperature excursion of less than 3 K. This figure is estimated from the associated changes in the differential resistance with this power applied and may be compared to the analysis further on in this chapter. In the case of o-TaS$_3$, the dissipated power was 100 times greater, 60 mW. The temperature rise within this sample was approximately 200 K this time deduced from the signal of the CDW phase transition present in the simultaneously measured resistance. In the examination of the model both these extremes are explored. For the purposes of calculation the cavity wall is set at 150 K.

5.3 Modes of Heat Dissipation

There are in general three modes of heat dissipation open to a warm fine-wire sample coupled to a cold cavity by means of helium exchange gas. These modes are Stefan-Boltzmann radiation, free convection and conduction. The scale of each mode's contribution to the overall heat dissipation in the sample is estimated in turn.

The radiative channel may be disposed of quickly owing to the microscopic surface area that the sample presents to the cavity. The radiation of power from the sample surface will follow the Stefan-Boltzmann law,
where \( e \) is the sample's emissivity, \( \gamma_{SB} \) is the Stefan-Boltzmann constant, \( A \) is the sample surface area and \( T_s \) is its mean temperature. The emissivity may lie from 0 to 1 but here the generous value of 1 is given to the sample surface.

In the case of NbSe\(_3\) a 0.6 mW power gives rise to about 3 K of temperature increase. The radiative contribution to the dissipation of power is 0.53 microwatts or less than 0.08% of the total 0.6 mW. For o-TaS\(_3\) the 100 K excursion resulting from 60 mW of applied power leads to a total radiated power of 180 microwatts. This contributes just 0.3% to the overall dissipated power. In either case the radiative contribution may be ignored.

Another mode for heat dissipation is by free convection. This is a complex situation to examine in detail. However, the scale of the convective contribution in relation to conduction may be estimated from analysis of the characteristic dimensions of the system. The Nusselt number, Nu, is defined as the ratio of the heat transfer by convection and conduction to that of conduction alone. As Nu approaches 1 the convective component of heat transfer becomes negligible [5.1]. The Nusselt number may be formed from the combination of two dimensionless groups, the Grashof number, Gr, and the Prandtl number, Pr. These are defined in the following manner,
\[ Nu = (Gr)^x \ (Pr)^y \quad (2) \]

where,

\[ Gr = \frac{d^3 \ B \ \Delta T \ g}{\nu^2} \quad (3) \]

and,

\[ Pr = \frac{C_p \ \nu}{k} \quad (4) \]

Here \( d \) is the width of the gas layer that separates the sample from the cavity wall with temperature gradient \( \Delta T \) and \( g \) is the acceleration of gravity. The helium exchange gas has cubical coefficient of expansion \( B \), kinematic viscosity \( \nu \), specific heat \( C_p \), density \( \rho \) and thermal conductivity \( k \). The exponents \( x \) and \( y \) are determined from the actual physical situation by experiment. The exponents \( x \) and \( y \) are not known for this geometry in helium gas. In order to make an estimate of the Nusselt number results from experiments in air are used [5.2]. These observations are drawn upon as a guide. For air, as in helium at low temperatures, the Prandtl number does not vary greatly. Attention is accordingly restricted to the Grashof number. In air a Grashof number of less than 1000 corresponds, in this geometry, to a Nusselt number of 1. Convection will therefore be negligible. Should the Grashof number rise to 2000 the convective contribution to heat transfer will amount to 5% [5.2]. These figures may be compared to experiments performed in helium at low temperatures, albeit with a different
geometry. For those experiments the onset of convection was found at a Rayleigh number, $Ra$, of $5.8 \times 10^3$. At a Rayleigh number of $10^4$ the convective contribution to the heat transfer was 10% [5.3]. The Rayleigh number is equivalent to the Grashof number multiplied by the Prandtl number,

$$ Ra = Gr \times Pr \quad (5) $$

For the experiments described in this chapter $Gr$, $Pr$ and $Ra$ are estimated with tabulated values where possible and with ideal gas values where precise information is lacking. The Prandtl number is found to be roughly 0.022. The Grashof number is found to follow,

$$ Gr = 283 \frac{(T_s - T_w)}{T_w} \quad (6) $$

In the case of the NbSe$_3$ experiments the temperature excursion of 3 K yields a Grashof number of less than 6. The corresponding Rayleigh number would be 0.125. The experiments performed on o-TaS$_3$ had a temperature rise of 100 K giving a Grashof number of less than 200 with a Rayleigh number of 3.7. By any of the estimations of the contribution of convection in relation to the conduction component of heat transfer may be ignored.

The conclusion that may be drawn from the calculations outlined above is that the primary channel for heat dissipation open to the fine-wire samples in this situation is that of direct conduction through the exchange gas to the cavity wall.

Heat conduction in a continuum is governed by Fourier's law, written here in a
form that reflects the cylindrical geometry of the model,

$$\frac{dT}{dr} = \frac{-P}{4\pi r k L}$$

(7)

where \( T(r) \) is the radial distribution of temperature in the gas measured from the centre of the wire sample, \( P \) is the power dissipated by the sample, \( 2L \) is the sample length and \( k \) is the thermal conductivity of the helium gas. Two assumptions are implicit in this expression. First, it is supposed that all the power put into the sample is taken up by the exchange gas. This will ignore the power drain to the cold boundaries but this is expected to be a negligible factor in this simplified model. The second assumption is that the axial temperature distribution in the exchange gas may also be ignored. For the purposes of the model it is imagined that the bulk of the sample length not near the cold boundaries is responsible for the heat dissipation in the sample. For this severe aspect ratio elements in the exchange gas not near the boundary are expected to be quite unaware of the latter's existence. To most of the gas the wire seems infinite.

The boundary conditions require that at the sample surface, \( r_s \), the temperature of the gas be the same as the sample while at the cavity wall, \( r_w \), it be equal to the temperature of the cavity wall,

\[
T(r_s) = T_s \quad \text{(8)}
\]

\[
T(r_w) = T_w \quad \text{(9)}
\]
It should be noted that steady-state conditions are assumed in this model. The justification for this lies in observations made on the samples and in estimates of the characteristic decay times for this model. In the case of experiments the dilation was closely examined for fixed quantities of power to determine whether or not a "relaxation" could be observed. Such a relaxation would indicate an approach to equilibrium on the part of the sample with respect to the temperature distribution along its length or radially to the gas. For time scales on the order of 0.03 seconds no such relaxation was ever observed. For the cylindrical geometry the characteristic decay time would follow,

$$\tau = \frac{C_p}{k} d^2 \quad (10)$$

For the geometry considered here the characteristic decay time would be roughly 0.1 seconds. Since the time scale of the active dilatometry experiments was approximately 1 second steady-state conditions may be assumed.

The simple formulation in equation 7 requires two modifications. One stems from the breakdown of Fourier's law in regions where the gas may not be treated as a continuum. The other arises from the temperature dependence of the helium's thermal conductivity.

Fourier's law is a continuum law and is applicable to the helium gas everywhere except in regions that lie a few mean-free-paths from the solid surfaces of either the cavity or the sample. Over these distances it is necessary to take explicit account of the discrete nature of the gas particles through the application of
kinetic theory. The effect of these considerations is a deviation from the expected temperature profile near the solid surfaces, a temperature "jump" [5.4]. The recovery of Fourier's law requires a re-positioning of the boundary conditions to radii immediately outside the temperature jump region and an estimation of the temperature of the gas at these points. The temperature jump effect is expressed in the equation,

$$\delta T = g \frac{dT}{dz}$$  \hspace{1cm} (11)

where $g$ is the "jump" distance and $dT/dz$ is the radial temperature gradient of the gas extrapolated to the solid surface. This latter figure can be estimated from Fourier's law (eq. 7) applied to the region of the temperature jump. The jump distance depends upon the details of the gas thermal conductivity and the condition of the solid surface. For clean surfaces, high temperatures and a light gas the jump distance is roughly one mean-free-path [5.5]. This figure is appropriate to the conditions within the model at both sample and cavity surface. Given this estimate of the jump distance the effect of the temperature jump within this system may be effectively ignored. The position of the "continuum" begins at a point 0.2% from the sample surface and 0.001% from the cavity surface. The temperature adjustment in the low power case is less than 0.3 mK while in the high power case this rises to only 0.03 K. In each example the temperature jump
effect may be neglected.

The temperature variation of the helium exchange gas thermal conductivity is a much more important effect. Over the temperature range from 100 to 300 K the thermal conductivity of the helium gas can be described empirically by a linear relation,

\[ k = k_0 + k_1 T \]

(12)

where \( k_0 = 0.0287 \text{ W/m-K} \) and \( k_1 = 0.000429 \text{ W/m-K}^2 \) [5.6] (the temperature variation of the thermal conductivity of a monotonic, non-interacting ideal gas is generally has a square-root dependence on temperature [5.4]). In the case of the NbSe\(_3\) experiments temperature excursions of 3 K mean a variation in the helium thermal conductivity of less than 1%, taken here as constant. However, for \( \alpha \)-TaS\(_3\) the temperature changes of 100 K or more mean that such a simplification is not possible. Including the temperature dependence of the thermal conductivity, Fourier’s equation is now written as,

\[ (k_0 + k_1 T) \frac{dT}{dr} = \frac{-P}{4 \pi r L} \]

(13)

with the boundary conditions described in equations 8 and 9. This differential equation is readily integrated with the boundary conditions to arrive at the solution,

\[ \frac{k_1}{2} (T_w^2 - T_o^2) + k_0 (T_w - T_o) = \frac{P \ln \left( \frac{r_w}{r_o} \right)}{4 \pi L} \]

(14)
This equation serves to define the way in which the sample rids itself of heat and is of great importance to the determination of the longitudinal temperature distribution within the sample. The relationship between the sample temperature and the power is expressed as,

\[ T_s = \sqrt{\left(\frac{k_2}{k_1} + T_w\right) - \frac{P \ln(r_2/r_1)}{2 \pi L k_1} - \frac{k_2}{k_1}} \] (15)

This equation is used to guide the analysis of experiments performed on o-TaS\textsubscript{3} carried out at high powers. In the low power regime, appropriate to NbSe\textsubscript{3}, the square-root in equation 15 may be expanded to find that,

\[ T_s = T_w - \frac{P \ln(r_2/r_1)}{4 \pi L k_1 \left(\frac{k_2}{k_1} + T_w\right)} \] (16)

5.4 Longitudinal Temperature Distribution in the Wire

Equation 14 defines the surface heat transfer experienced by a sample whose temperature is very much higher than the walls of the cavity in which it lies. It is in marked contrast to Newton's law of cooling which predicts a linear relationship between the power and the temperature gradient. This is a consequence of the temperature variation of the thermal conductivity of the helium gas. In effect it becomes more difficult to maintain a gradient of temperature between the wire
sample and the cavity as the thermal conductivity of the gas rises, hence the weaker dependence upon the dissipated power. However, this formula is only an approximation and is intended only as a guide for an empirical conversion of the dissipated power into temperature later on in this chapter. The use of this form of the surface dissipation of heat results in a differential equation which is non-linear and not solvable in closed form. To gauge the temperature distribution in the hot wire the Newtonian form is used for the dissipation of heat, that is a linear relationship that assumes that the thermal conductivity of the exchange gas remains constant as the wire becomes hot. This will be valid for small temperature excursions.

Following the example of the arguments above the model's behaviour is examined in the steady-state case only. This is a consequence both of the experimental evidence for equilibrium on a time scale much smaller than the time scale of the active dilatometry experiments and estimations of the characteristic relaxation times for these metallic samples. For example, the characteristic relaxation time for NbSe₃ near 100 K may be estimated from its specific heat, thermal conductivity and length from equation 10. The specific heat is 9.3 R₀ or 1.5 MJ/m³-K [5.7], while its thermal conductivity is 25 W/m-K [5.8]. With a length of 6 mm the relaxation time is roughly 2 seconds. Since the experiment is carried out on the time scale of seconds steady-state conditions are assumed to exist.

The longitudinal distribution of temperature in the fine-wire sample will follow Fourier's law with a Newtonian surface dissipation of heat,
\[ V K \frac{d^2 T_z}{d z^2} = \frac{4 \pi L k_o}{\ln(r_s/r_w)} (T_w - T_s) - P \] 

where the sample has volume \( V \), and thermal conductivity \( K \). The boundary conditions for this equation are,

\[ T_s(-L) = T_w \quad (18) \]
\[ T_s(+L) = T_w \quad (19) \]

corresponding to the points where the sample is thermally anchored to the probe. The solution to this equation is,

\[ T_s - T_w = -\frac{P \ln(r_s/r_w)}{4 \pi L k_o} \left[ 1 - \frac{\cosh(\gamma z)}{\cosh(\gamma L)} \right] \quad (21) \]

where,

\[ \gamma^2 = \frac{4 \pi L k_o}{\ln(r_s/r_w) V K} \quad (22) \]

A calculation of \( \gamma \) yields a value of roughly \( 10^4 \text{ m}^{-2} \). This gives the distribution of temperature a very sharp drop near the ends where it is anchored. In figure 5.3 this distribution is shown for the parameters used above in NbSe\(_3\). It should
Figure 5.3 Calculated temperature profile in a fine wire sample.
be noted that approximately 94% of the sample is within 10% of the maximum temperature. The results from the higher temperature equation are not expected to be much different. In fact, it is expected that the temperature variation of the exchange gas thermal conductivity will work to further sharpen this distribution.

5.5 Experiments on NbSe$_3$

The NbSe$_3$ used in these experiments was grown at Dalhousie University by the HVT technique. The characterization and description of this material and its phase transitions are detailed in the chapter on materials. A sample drawn from the lot # 1018 was mounted in the cantilever mode using a lever fashioned from a loop of .005 " o.d. The sample was 7.10 mm long in the b axis direction, 20 microns wide in the a axis direction and 10 microns wide in the c axis direction (+/- 10 microns). The lever used was 4.51 mm long with a mechanical bias at room temperature of 470 microns. This corresponded to a uniaxial strain of 50 MPa, sufficient to depress the upper 144 K CDW phase transition by 0.2 K [5.9].

After mounting, four-point resistivity contacts were made with 25 micron o.d. gold wire and silver paint. The gold wire was weak enough mechanically to place little or no additional strains on the molybdenum lever. Finally, a small flake of well-cleaved HOPG was glued to the lever near the sample and electrical contact made to it with another 25 micron gold wire.

After all the relevant dimensions of the sample and the lever were measured with a travelling microscope the gallows assembly was mounted on the lower,
flexible capacitor plate with a small amount of varnish. Before being sealed in the vacuum cans the tunnelling tip was brought to within 10 microns of the HOPG surface by means of the coarse mechanical approach. The probe was sealed and evacuated to .05 torr and then helium exchange gas introduced in the cans to a pressure of roughly 100 kPa. The probe was placed in the inner dewar that was suspended from the ceiling by shock cords and the inner dewar suspended in a bath of liquid nitrogen. After the temperature stabilized at about 80 K the external heaters were activated and a temperature drift of 3 K/hr achieved. Shortly afterwards a tunnelling approach was made and the computer was allowed to take over the experiment. The differential resistance of the sample was monitored by means of a phase-locked-loop technique with an excitation voltage amplitude of 100 mV at a frequency of 336 Hz.

Within the original conception of this "active" dilatometry technique the sample’s differential resistance was to be the sole measure of its temperature. In order to maintain a proper interpretation of the differential resistance care was taken not to cross the threshold electric field for this material. This restricted the maximum voltage that could be applied to the sample and limited the maximum power dissipated in the sample to less than 0.6 mW. Consequently, temperature excursions were confined to 3 K or less. A complete measurement of the dilation over the 100 K region of interest therefore required 30 or more separate measurements suitably spaced in temperature. For the purposes of this discussion each one of these separate experiments is called a "trial". The steps that make
up an individual "trial" are detailed below:

(i) The sample, with no DC voltage applied, is assumed to be in thermal equilibrium with the probe and its diode thermometer. A measurement is made of the sample's differential resistance and this is recorded against the temperature of the probe.

(ii) A digital-to-analog converter (DAC) following instructions issued by the computer raises the voltage across the sample by approximately 1.5 mV. This value is held while measurements are made of the sample voltage, DC current, differential resistance and dilation. These measurements are recorded by the computer. The DAC again raises the voltage by another 1.5 mV increment and the measurement series is repeated. The computer continues this cycle for 200 steps upward in voltage followed by 200 steps downward to zero. Each step is limited by the reading time of the instruments, roughly 1 second, and the entire "trial" takes about 5 to 6 minutes to complete. The temperature drift of the dilatometer is 3 K/hr limiting the overall temperature resolution to 0.2 K.

(iii) With the sample again at zero DC volts the differential resistance is measured and recorded with the probe temperature. This completes a single "trial".
Once a trial is complete the computer monitors the temperature until the probe has increased its temperature by 2 to 3 Kelvin. At this juncture a new "trial" is begun. The experiment ends when the probe temperature has drifted well above the phase transition.

An example of the results of a single trial is shown in figure 5.4. Here the absolute dilation and the differential resistance are plotted as a function of the electric field applied to the sample. This figure includes data gathered with both a rising and a falling electric field. Little or no hysteresis appears between the forward and reverse measurements of the absolute dilation. This indicates that the drift rate of the probe in combination with the cell expansion is negligible on the scale of this trial. In addition, the lack of hysteresis supports the assumption of steady-state conditions on the time scale of these measurements. The differential resistance rises gradually with the electric field but otherwise displays none of the unusual characteristics that would be associated with the threshold electric field. Thus, no distinction need be drawn between the zero-electric-field differential resistance and the values measured in the "trial" at finite electric field. This ensures the reliability of the conversion of differential resistance into temperature undertaken further on in this discussion.

5.5.1 Conversion of Differential Resistance into Temperature

The first step in the analysis of the NbSe$_3$ data is the conversion of the
differential resistance into temperature. This is accomplished through the construction of the "interpolation" curve illustrated in figure 5.5. The data plotted in this interpolation curve is that drawn from the individual trials where the sample was in thermal equilibrium with the probe (steps (i) and (iii) in section 5.5). The data is shown with the resistance on the abscissa in order to emphasize the purpose of this figure: the conversion of resistance into temperature.

The conversion from differential resistance into temperature is performed by the method of linear interpolation. First, a differential resistance value is read from the data of a single "trial". The interpolation curve in figure 5.5 is consulted in order to find the two resistance values which lie on either side of the trial's differential resistance. A straight line is drawn through the two bracketing points in order to define a linear interpolation between them. The resulting equation is used to determine the temperature that corresponds to the trial's resistance.

It is clear from this figure that difficulties will be encountered between 130 and 150 K. In the first case the interpolation data is triple-valued in this temperature range owing to the CDW phase transition. However, the most important problem encountered in this temperature range lies in the error of the interpolation attempted near the turning points at 130 and 150 K. The error of the interpolation may be established from the slope of the line used to convert the resistance data. This slope is multiplied by the intrinsic fluctuations present in the differential resistance data to yield an estimate of the temperature error (in the case of these experiments on NbSe₃ the intrinsic fluctuations in the resistance
Figure 5.4 Results of a single trial for NbSe$_3$ showing the dilation and differential resistance changes as a consequence of Joule heating.
were less than 0.05 ohms). As the interpolation nears the turning points at 130 K and 150 K the slope rises precipitously and the error in the conversion to temperature renders the data in these regions unreliable.

An example of this technique of Resistance Conversion to Temperature (RCT) may be found in figure 5.6. This figure shows three individual "trials" spaced at 2 K intervals between 96 and 100 K. The dilation is plotted as function of the temperature as derived from the differential resistance signal. The temperature excursions are seen to be roughly 2 K for a dissipated power of 0.6 mW. These dilation results, it must be emphasized, are absolute measurements as the temperature of the probe is almost constant over the duration of these "trials". The calculation of the absolute coefficient of thermal expansion proceeds directly from the slopes of these curves.

The coefficient of thermal expansion derived from the slopes of RCT dilation data for NbSe₃ is shown in figure 5.7. The slopes are calculated from least-squares-fits (LSF) to dilation data similar to that shown in figure 5.6. The data includes the results of two separate experiments on the same sample. The second, repeat experiment is somewhat noisier than the first run owing to deteriorating tunnelling conditions. These unstable conditions may be ascribed to impurities that collect between the tip and the surface of the HOPG or to damage to the HOPG surface itself. There is no way to improve this situation short of withdrawing the probe and re-setting the position of the tunnelling tip.

From figure 5.7 there is seen to be a gradual rise in the thermal expansion from
Figure 5.5 Resistance-temperature interpolation data for NbSe$_3$. 
a value of approximately 4 ppm/K near 100 K to 5.5 ppm/K near 125 K. Between 125 K and 155 K the thermal expansion is subject to large swings (sometimes becoming negative). This is not due to any inherent instability in the raw dilation data (as will be found later in this chapter) but stems from the difficulties encountered in the RCT scheme near the turning points around 130 and 150 K.

5.5.2 Conversion of Dissipated Power Into Temperature

The utility of the resistance conversion to temperature scheme is severely limited by the enormous errors encountered near resistance turning points. In order to establish a temperature scale for the dilation measurement in these regions appeal is made to the quantity of power dissipated by the sample.

The power dissipated by the sample is calculated from the recorded values of the voltage and DC current. In figure 5.8 the temperature is shown as a function of the electrical power dissipated by the sample near 95.8 K. The temperature scale used in this illustration is that derived by the RCT scheme. This is expected to be a reliable conversion because it lies outside the temperature range between 130 and 150 K. Clearly, in the case of small power levels and the consequent small temperature excursions the relationship between sample temperature and power is linear. This confirms the spirit of the analysis in section 4.3 which predicted a Newton's law-type cooling for small power levels.

In any event the mathematical analysis is expected only to provide a framework
Figure 5.6 Absolute dilation plotted against resistance-interpolated-temperature for three trials performed on NbSe$_3$.
Figure 5.7 Absolute coefficient of thermal expansion for NbSe$_3$ employing the resistance-interpolated-temperature scale. The two symbols correspond to two separate experiments performed on the same sample.
for a phenomenological treatment of the data. Here it is assumed that the relationship between the power and the temperature of the sample is linear throughout the temperature between 100 and 200 K. While it is true that the sample is undergoing a phase transition from the ICDW to the normal state the surface cooling coefficient, upon which the analysis is based, is a function only of the dimensions of the sample and the properties of the gas. Thus, it is not expected to be sensitive to the sample's internal state. By using those "trials" that lie outside the temperature region between 130 and 150 K a series of curves like that shown in figure 5.8 may be constructed where temperature is linearly related to power. The slopes of these curves, dT/dP, relate the power directly to the sample temperature since the starting, or zero power temperature is known from the initial measurement of the probe temperature (step (i) in section 5.5).

Motivated by the details of the mathematical treatment in section 5.3, in particular by equation 16, these dT/dP values are shown against \((T_w + k_o/k_1)^{-1}\) in figure 5.9. The LSF also shown in figure 5.9 provides a reasonable fit to the data with a slope of 4.0 (+/- .4) x 10^5 K^2/W and an intercept of 840 (+/-160) K/W.

With this regression in hand the entire "trial" sets for NbSe_3 are re-evaluated from the point of view of the dissipated power. The result of the Power Conversion to Temperature (PCT) is shown in figure 5.10 where the absolute dilation is given as a function of the temperature. The data points for each trial are calculated from the regression in equation 23. Then, trials are brought into coincidence by a vertical off-set where their temperatures overlap. Where
Figure 5.8 Variation of resistance-interpolated-temperature with the dissipated power for NbSe$_3$.
temperatures do not overlap an extrapolation is made between the two adjacent trials. The largest extrapolation distance was less than 0.2 K. In this manner a continuous record of the absolute dilation was fashioned. The CDW phase transition near 145 K is clearly resolved in both the upper and lower curves. The lower curve is the first experimental run while the upper is the repeat run. The noise level in the second is greater than the first for the reasons alluded to in section 5.51. The vertical displacement of each is of course arbitrary and does not affect the calculation of the expansion coefficient.

The calculation of the coefficient of thermal expansion proceeds along the same lines as above: individual trials are examined and a LSF is applied to the data of a complete trial to arrive at the slope of the dilation versus temperature. Data gathered on the rising electric field is treated separately from data gathered in falling electric fields. In practice, with a very small drift rate in the probe, the two calculations tend to overlap. The temperature associated with each slope calculation is the centre point of the temperature data. The full absolute dilation curve in figure 5.10 is not suited to the calculation of the thermal expansion since the "joined-up" trials present small discontinuities in the data which translate into large noise levels in the slope calculation.

The coefficient of thermal expansion is shown as a function of temperature in figure 5.11. In the first place the data in figure 5.10 should be compared to the data in figure 5.7. The latter is the result of a resistance conversion to temperature and so should substantially agree with the power conversion to
Figure 5.9 Change in sample temperature for a fixed quantity of electrical power as a function of the inverse ambient temperature in NbSe$_3$. 
temperature outside the temperature range between 130 K and 150 K. The PCT scheme reveals a discontinuity in the thermal expansion near the phase transition of approximately +1.8 ppm/K to within 12%. Such a discontinuity would be typical of a second order phase transition and is thus consistent with the observed order parameter behaviour for NbSe$_3$ as deduced from the integrated peak intensities of X-ray scattering studies [5.10].

Immediately below the phase transition there does seem to be some evidence for a precursor "dip" in the thermal expansion. This is most pronounced in the first run where the noise levels in the electron tunnelling signal were rather smaller than in the second experiment. Such a precursor might be expected in this material in light of the recent experiments performed by Hauser et al. on the quasi-one-dimensional CDW compound "blue bronze" (K$_3$MnO$_3$) [5.11]. In these results the thermal expansion was measured as a function of temperature by means of a standard capacitance dilatometer (although blue bronze is quasi-one-dimensional it forms a more robust single crystal than those of the TMT class). In the measurements is seen a precursor dip in (100) and (001) crystal directions as well as a precursor "rise" in the chain direction (010). Unfortunately, the resolution of the NbSe$_3$ data is not sufficient to allow the application of the 3 dimensional X-Y fluctuation model that Hauser et al. use to examine their data. Moreover only chain direction measurements are available for the compounds studied in this chapter. This also means that an estimation of the anisotropic Gruneisen parameter cannot be made. For the monoclinic crystal system appropriate to
Figure 5.10 Absolute dilation as a function of temperature for NbSe$_3$.

Temperature calculated from the power consumed by the sample.
Figure 5.11 Absolute coefficient of thermal expansion as a function of temperature for NbSe$_3$. Thermal expansion calculated from the power consumed by the sample. The two symbols correspond to two separate experiments performed on the same sample.
NbSe$_3$ there are 13 independent elastic constants and 4 independent thermal expansion tensor components. Only two of the former have been measured and only one of the latter. Thus, a calculation of the anisotropic Gruneisen tensor for this compound cannot be undertaken with the available information.

5.5.3 Results near the CDW phase transition

A trial which overlaps the region of the CDW phase transition can provide a detailed accounting of the dilational changes associated with this transition. In addition, such a trial can aid in establishing the validity of the PCT interpolation from 130 to 150 K as shown in figure 5.9.

Figure 5.12 shows the raw data for one of the trials that ought to overlap the CDW transition. The figure shows the absolute dilation plotted as a function of electrical power and the trial begins at a temperature of 143.18 K. The position of the phase transition in this data may be deduced by subtracting an arbitrary linear background from the data in order to emphasize discontinuities in the dilation. This is done in figure 5.13. The presumed position of the CDW phase transition is found at 580 (+/- 20) microwatts. This figure may be compared to the differential resistance measured simultaneously and shown in figure 5.14. The onset of the normal state clearly begins near 580 microwatts and is consistent with the resistance figures measured previously and shown in the Materials chapter.

The temperature of the phase transition may be deduced from the resistance
measured as a function of temperature as shown in figure 5.5. In a plot of the negative logarithmic derivative of the resistance with respect to temperature the peak conventionally determines the position of the phase transition as illustrated in figure 5.15. This is found to be 144.8 (+/- 0.2) K and additionally confirms that the quantity of stress applied to the sample is not enough to significantly depress transition temperature. Within the assumption of a linear variation of temperature with power the value of dT/dP at 143.18 K is found to be 2800 (+/- 300) K/W. This compares favourably with the regression estimate from equation 23 of 2700 (+/- 350) K/W and tends to affirm the validity of the previous analysis.

With a figure of 2800 K/W the conversion from power to temperature proceeds quickly. Shown in figure 5.16 is the absolute dilation as a function of the temperature. It may seen that the overall background thermal expansion is 7.1 ppm/K. This accounts for the points that occupy the discontinuity at the phase transition near 145 K in figure 5.11. The value of the slope change deduced with this background removed is + 1.8 (+/- .2) ppm/K in agreement with the figure derived from the absolute coefficient of expansion in figure 5.11.

5.5.4 Effect of Elastic Compliance Changes at the Transition

When the absolute dilation is measured in the cantilever mode some ambiguity may attend the results. This is because a finite quantity of uniaxial strain is applied in the same direction as the dilation measurement. It is usual for elastic
Figure 5.12 Absolute dilation of NbSe$_3$ in the vicinity of the CDW phase transition placed against the consumed power.
Figure 5.13 Dilation of NbSe$_3$ near the CDW phase transition with a constant linear background subtracted. Viewed as a function of the consumed power.
Figure 5.14 Differential resistance on NbSe$_3$ near the CDW phase transition as a function of the consumed power.
Figure 5.15 Logarithmic derivative of resistance with respect to temperature versus temperature for NbSe$_3$. 
compliance changes to accompany the CDW transition and these will alter the length of a sample under strain. In order to make a final pronouncement on the zero strain length changes associated with the phase transition there must be an accounting of the compliance effects. The geometry of the cantilever mode allows the compliance component of any length change to be expressed as,

\[
\frac{\Delta L}{L} = \frac{\eta \Delta Y}{Y^2} \left( 1 - \frac{\Delta Y}{Y} \right)
\]

(25)

where \(\eta\) is the uniaxial strain, \(Y\) is the Young's modulus, \(\Delta Y\) is the change in the Young's modulus and \(\Delta L/L\) is the fractional length change detected by the dilatometer. The uniaxial strain on the sample near its phase transition may be estimated from the depression of the phase transition. In the materials chapter the zero strain phase transition is 144.9 (+/- 0.1) K. The depression of the phase transition was determined to be 144.8 (+/- 0.1) K. This yields a maximum depression of 0.3 K. The depression of the upper phase transition with uniaxial strain is - 4.4 K/GPa to within 2%. The maximum strain felt by the sample is consequently 80 MPa which is close to the room temperature estimate of 50 MPa. The relative change in the Young's modulus is approximately 300 ppm at the upper transition and the absolute modulus is roughly 150 GPa [5.12]. Together, these yield a compliance contribution to the dilation of 0.17 ppm which is three times smaller than the noise level in these experiments. The compliance contribution is justly regarded here as negligible.
5.5.5 Experiments near the 59 K CDW transition

The lower CDW transition was not accessible to the tunnelling dilatometer. Attempts were made to extend measurements of the dilation to below 59 K but all these ended in failure. The reason for this lay in the sharply reduced sensitivity of the piezoelectric actuators at liquid helium temperatures. The operation of a dilatometer requires thermal equilibrium throughout the probe in order to make proper experiments. Thus, the first step in extending measurements below 77 K was the cooling of the probe to 4.2 K after which a slow drift upwards was established. However, all mechanical approaches at these temperatures ended with the tunnelling tip "crashing" into the HOPG surface. This was a direct consequence of a dramatic loss of sensitivity in the piezoelectric actuators. The only way that the mechanical advancement can work in this system is if its smallest increment of displacement is smaller than the full range of the piezoelectric actuator. Near 77 K the full range of the piezoelectric actuator is still 3 microns while the mechanical advancement can move 1 micron reliably. However, the full range of the piezoelectric actuator falls to 0.1 micron at 4.2 K, too small to be of any use. Moreover, this is usually seen as a symptom of the irreversible failure of the piezoelectric assembly. This is due either to a glue-joint failure or to the development of cracks in the piezoelectric tubes. It is unlikely that it is due to the intrinsic loss of sensitivity for this material at low temperatures. According to recent measurements there is very little additional loss in sensitivity between 77 K and 4.2 K [5.28]. In any case an approach for tunnelling cannot be made and the
Figure 5.16 Absolute dilation of NbSe$_3$ as a function of temperature calculated from the consumed power.
probe is usually damaged in these attempts. Consequently, experiments at temperatures below 77 K were abandoned.

5.5.6 Discussion of NbSe$_3$ Thermal Expansion Results

The coefficient of thermal expansion of NbSe$_3$ clearly shows a step discontinuity at the 145 CDW phase transition which amounts to +1.8 (+/-0.2) ppm/K. A detailed examination of the dilation in the transition region yields little evidence for a fluctuation contribution to the thermal expansion. Consequently, the phase transition here will be treated within the framework of the Ehrenfest relations at $T_C$.

The measured anomaly in the specific heat of NbSe$_3$ is shown in figure 5.17 which follows the data of Tomic et al. [5.7]. Using a simple extrapolation about $T_C$ the discontinuity in the specific heat is calculated to be +0.4 R$_o$ or +64 (+/- 5) kJ/m$^3$-K. This is close to the value that Lear et al. extract of 72 kJ/m$^3$-K for the same data [5.9]. The ratio of the discontinuities in thermal expansion and specific heat is equivalent to the negative logarithmic derivative of the transition temperature with respect to a uniaxial stress applied in the same direction as the expansion measurement. This ratio is calculated here as -0.028 (+/-0.003) GPa$^{-1}$. The value measured by R.S. Lear and co-workers is -0.0310 (+/-0.0005) GPa$^{-1}$ and is in agreement with the value deduced from the mean-field steps above [5.9].

On the other hand, the relative discontinuity in the elastic modulus deduced
Figure 5.17 Specific heat of NbSe$_3$ near the CDW phase transition. Drawn from reference 5.7.
from any pair of the three measurements considered above is \( \Delta E/E = -0.0012 \) to within approximately 10% (assuming a Young’s modulus of 150 GPa [5.12]).

The step measured by the vibrating-reed technique is \(-3.3 \times 10^{-4}\) which is smaller than the calculated value by a factor of nearly 4. It may be pointed out here that these elastic modulus changes would contribute at most a discontinuity of 1 ppm to the measured dilation signal - barely above the noise level of this measurement.

Thus, it is found that the steps in the coefficient of thermal expansion and the specific heat along with the uniaxial stress dependence of the CDW transition temperature combine in a self-consistent manner under the Ehrenfest relations at \( T_c \). The modulus of elasticity as measured does not fit into these relations being 4 times smaller than the predicted value. It may be suggested that a source of this discrepancy may lie in the use of different NbSe\(_3\) samples in estimating these physical properties. For example, in the vibrating-reed experiments of Brill two samples of the same lot have a moduli of elasticity that differ by a factor of 3.7 [5.12]. This happens to be roughly the same variation between predicted and measured values of the modulus discontinuity at the phase transition. While the variation in itself proves nothing in this particular discussion, the magnitude suggests that such variations may be expected for these materials.

5.5.7 Anharmonic model of CDW thermal expansion

In their paper on the thermal expansion of the quasi-one-dimensional
compound blue bronze (\( K_{0.3}MnO_3 \)) M.R. Hauser et al. propose a one-dimensional anharmonic model of the CDW phase transition. The model is composed of \( N \) identical masses linked together by identical springs of rest length, \( L_0 \). The potential energy of this system, when subjected to a small displacement \( x \), is given by the Maclaurin series,

\[
U_s = N \left[ e_s x + \frac{f_s}{2} x^2 + \frac{g_s}{6} x^3 + \frac{h_s}{24} x^4 + \ldots \right] \quad (26)
\]

The inclusion of terms with orders higher than 2 makes this an anharmonic interaction and so yields a non-zero thermal expansion coefficient. Without loss of generality, \( e_s \) is taken as zero. Conditions of stability require that \( g_s \) be less than 0. The identification of \( f_s \) with the spring constant makes this term positive.

The transition to the CDW state is brought about through the conventional route of dimerization. Successive pairs of masses move slightly closer together so that the rest length of the springs alternates between \( L_0 - a \) and \( L_0 + a \). The factor "\( a \)" may be called the dimerization parameter and generally in these CDW systems will follow the temperature dependence of the order parameter,

\[
a = a_o \left( \frac{T - T_c}{T_c} \right)^{1/2} \quad (27)
\]

for all \( T < T_c \). The term "\( a_o \)" represents the saturation value of the dimerization at \( T = 0 \). If "\( a \)" and the small displacement "\( x \)" are considered on the same footing then the potential energy of the dimerized chain may be easily calculated,
\[ U_D = N \left\{ \frac{g_s a^2}{2} x + (f_s + \frac{h_s a^2}{2}) x^2 + \frac{g_s}{6} x^3 + \frac{h_s}{24} x^4 + \text{constants} \right\} \]

The temperature dependence of the length of a one-dimensional lattice with quartic interactions has been calculated by Leibfried and Ludwig [5.27]. This temperature dependence follows,

\[ L(T) = L_0 + \frac{\Lambda_3}{2 \Lambda_2} \theta \quad (29) \]

where \( \Lambda_3 \) is the coefficient of the cubic term in the potential and \( \Lambda_2 \) is the coefficient of the square term. The factor \( \theta \) is the mean thermal energy per mode of the lattice in its harmonic approximation. Temperatures in the vicinity of \( T_C \) are sufficiently warm to allow \( \theta \) to be replaced by the one-dimensional classical value, \( k_B T \). Taken altogether, these foregoing considerations reveal that the discontinuity in the coefficient of thermal expansion at the CDW phase transition should amount to,

\[ \Delta \alpha = \alpha_s - \alpha_D = -\frac{g_s a^2}{2 f_s T_C L_0} \quad (30) \]

to lowest order in the interaction \( h_s \). Recalling that \( g_s < 0 \) and that \( f_s > 0 \) this implies that there should be a positive discontinuity in the thermal expansion at \( T_C \).

The question of whether or not a real CDW system may be described by this model is a subtle one. Real physical CDW compounds are three-dimensional.
objects with chain-to-chain interactions that are not included in this model. Also, the periodic lattice distortion in real systems may not be simply described by a dimerization in the chain direction. After all, the CDW state is an electron-phonon system and the PLD will depend crucially on the shape of the Fermi surface. With this said, perhaps NbSe$_3$ is as good a candidate for comparison as may be expected. Although NbSe$_3$ is less quasi-one dimensional than say o-TaS$_3$, the PLD is in fact confined to the chain axis which could allow it to be treated as a dimerization (albeit with a large effective chain mass). Thus, the positive step in the thermal expansion that is measured in these experiments may support the anharmonic model described above in a limited manner.

5.6 Experiments on o-TaS$_3$

The samples used in these experiments were all selected from the growth lot # 1354 produced at Dalhousie University by the halogen vapour transport technique. A complete characterization of this lot may be discovered in the materials chapter. Three samples were used in these experiments corresponding to three different degrees of uniaxial strain. It was hoped that in this way any Young's modulus changes present near the CDW phase transition could be detected and separated from the simple thermal expansion effects.

The electrical properties of o-TaS$_3$ require a modification of the experimental procedure outlined above in section 5.5 for NbSe$_3$. This modification amounts to
a large increase in the maximum voltage applied to the sample. Instead of rising in steps of 1.5 mV these are increased in these experiments to approximately 35 mV. Otherwise the procedure was identical. The use of such large electric fields in the experiments has two purposes. The first of these is to stimulate enough Joule heating in the sample to cause it to expand significantly. However, the fields used here go much further than this; when an experiment is begun it is hoped that the quantity of power used will be sufficient to heat the sample across its CDW phase transition. The voltages required to do this are typically established in preliminary trials at low temperatures before the experiment begins. Such an exploratory trial is shown in figure 5.18 where the dilation and differential resistance are measured as a function of voltage across the sample. The onset of non-ohmic conduction is undetectable on such a large voltage scale. The dramatic signature in the dilation near 9 volts is accompanied by a similarly striking shift in the differential resistance. This is interpreted as the onset of the normal state from the CDW state in o-TaS₃.

The necessity for this large increase in voltage lies in the fundamental electrical properties of o-TaS₃. In the first place the resistance of this material in its CDW state is very high, tens of kilo-ohms. This is due to the onset of a Peierls insulator state below the phase transition. Unlike NbSe₃, o-TaS₃ has no "metallic" chains that remain unaffected by the CDW state. The high values of the o-TaS₃ resistance may be viewed in contrast to the values present in the NbSe₃ which are two orders of magnitude lower. This means that in a similar voltage controlled
Figure 5.18 Dilation and differential resistance of o-TaS$_3$ as a function of electric field.
experiment the quantity of dissipated power would be reduced by a factor of 100. Coupled to this diminution of the power is the difficulty raised by the low value for the threshold electric field in this lot of \(\text{o-TaS}_3\). In order to raise the temperature of \(\text{NbSe}_3\) it was possible to apply nearly 300 mV and still be well away from the threshold field in this material. By comparison, the threshold fields in \(\text{o-TaS}_3\) are almost an order of magnitude smaller. Thus, it is clear that the production of significant temperature changes in \(\text{o-TaS}_3\) will require the use of electric fields far in excess of the threshold for this material. This means that a resistance conversion to temperature cannot be applied to the data. Once threshold is crossed the differential resistance measured by the phase-locked-loop loses its meaning as the resistance of the sample: now it is only a measure of the local derivative of the I/V curve. The CDW "super-current" portion of the total current is known not to carry any entropy [3.46]. In addition, it may be noted in passing that the slope of the resistance versus temperature curve for \(\text{o-TaS}_3\) is quite small near the CDW phase transition. Hence, the conversion of resistance into temperature near the transition (assuming that such a measurement was possible) would include an absurdly large uncertainty stemming from the shape of the resistance curve. Instead, the analysis of the dilation data gathered in these experiments is made by an appeal to the dissipated power alone.
5.6.1 Temperature conversion by dissipated power in o-TaS₃

The conversion of dissipated power into temperature is guided by the results of the model investigations in section 5.3. In particular, attention is drawn to equation 15 which relates the temperature of the sample to the power when the exchange gas is allowed a linear variation with temperature. This equation may be cast in an empirical form as,

\[ T_g = \sqrt{\left( \frac{k_o}{k_1} + T_w \right)^2 + A P - \frac{k_o}{k_1}} \]  

where all the coefficients on the right hand side are known save 'A'. 'A' may be calculated by the inversion of equation 31 when the temperature of the phase transition is known along with the quantity of power required to bring the sample to this temperature,

\[ A = \frac{(T_C + \frac{k_o}{k_1})^2 - (T_w + \frac{k_o}{k_1})^2}{P_c} \]  

where \( T_C \) is the transition temperature and \( P_c \) is the quantity of power required to produce this temperature. With 'A' calculated the conversion of power into temperature may proceed. The parameter 'A' is phenomenological and as such may be expected to exhibit a temperature dependence. Thus, 'A' is calculated
separately for each trial examined.

The calculations above require a precise determination of $P_C$. The use of anomalies in the dilation signal to determine $P_C$ is tempting but the interpretation of such a scheme is ambiguous. Rather, the DC resistance is used to provide a independent estimation of $P_C$. Figure 5.19 illustrates this procedure. In this figure the negative logarithmic derivative of the DC resistance with respect to power is shown as a function of power. The DC resistance is calculated from the ratio of the sample voltage to the DC current. This graph is considered appropriate since the power is expected to behave roughly like the temperature. It follows that $-\frac{d(\ln R_{DC})}{dP}$ will be similar to the conventional representation used in finding the CDW transition, $-\frac{d(\ln R)}{dT}$. A peak in this graph fixes the position of the phase transition. Such a peak is seen in figure 5.19 which moreover displays the characteristics expected of $-\frac{d(\ln R)}{dT}$ versus $T$. The position of this peak is $P_C$.

To complete the calculation of $\Delta T$ the transition temperature must be known. This is most easily found by direct measurement. Figure 5.20 shows $-\frac{d(\ln R_{DC})}{dT}$ as a function of $T$. This data is extracted from the full series of trials that make up the high strain experiment on $\alpha$-TaS$_3$. The DC resistance is calculated from the first measurements of voltage and DC current (the sample will not have warmed significantly and the electric field will still be smaller than the threshold). The peak in the curve and hence the phase transition is positioned at 193.5 (+/-0.5) K. (This happens to correspond to a uniaxial strain of .51 %).

The conversion to temperature as shown above is dependant on the mode of
Figure 5.19  Logarithmic derivative of resistance with respect to consumed power in o-TaS$_3$. 
heat dissipation being primarily direct conduction through the exchange gas. Crude attempts to verify this in the probe were not successful, although it is difficult to say whether this was due to the verification procedure or the theoretical description adopted. In any case it is fair to include some mention of a convection-dominated model for heat dissipation. The principle difference between the conduction and convection dominated heat dissipation is that the latter sees the recovery of the empirical Newton's Law of cooling. Thus, the power may be converted to temperature by a square-root expression (eq. 34) or a linear one (roughly equivalent to eq. 16). Figure 5.21 shows the result of using these two conversions on a single trial in the o-TaS$_3$ experiments. As expected, the linear conversion will stretch the temperature scale out. The linear scheme also removes any curvature present in the dilation. The phase transition appears as a simple discontinuity in the slope of this curve. Although it is not wise to assume anything about the coefficient of thermal expansion of o-TaS$_3$ it does seem odd that this quantity would be constant over such a large range of temperature. By way of contrast, NbSe$_3$ shows a gradually increasing thermal expansion which appears more physical. With this said, the ensuing discussion will use the expression in equation 35 exclusively and assume conduction-dominated heat dissipation as is suggested by the Grashof and Prandtl numbers in section 5.3.
Figure 5.20 Logarithmic derivative of resistance with respect to temperature for \(\alpha\)-TaS\(_3\) suffering two different uniaxial strains.
5.6.2 Description of Samples

As mentioned, three samples were investigated in these experiments on o-TaS$_3$. These may be conveniently referred to as the "low", "medium", and "high" strain samples.

The sample with the least uniaxial strain was a single crystal 6.28 (+/-0.01) mm long. The cantilever used was fashioned from a loop of 0.002" o.d. molybdenum wire and carried an effective spring constant of 3 N/m. The room temperature mechanical bias of this lever was 48.1 microns. The depression of the CDW phase transition due to the application of uniaxial strain may be seen in figure 5.20. The transition was found at 215.0 (+/-0.25) K which leads to a uniaxial strain of 9.0 (+/-0.1) x 10$^{-4}$ in the vicinity of the phase transition. The dilation of the sample during a typical trial was in the range of 5 microns. Thus, this estimate of the strain could be reduced by approximately 10% over the course of a single trial.

The sample suffering a "medium" strain was 6.98 (+/-0.01) mm long. For this experiment the cantilever was made from a loop of 0.004" o.d. molybdenum wire with an effective spring constant of 50 N/m. The room temperature mechanical bias was 130 microns. The phase transition of this sample was discovered at 210.5 (+/-0.25) K which implies a uniaxial strain of 1.8 (+/-1) x 10$^{-3}$ near $T_C$. The expansion of the sample during a dilation trial was roughly 7 microns so that a reduction of 5% in the strain might be expected over a typical trial.

The final sample, 7.18 (+/-0.01) mm long, experienced a "high" value of uniaxial strain. The cantilever was constructed from a strip of 0.005" phosphor-bronze 0.95
Figure 5.21 Absolute dilation of α-TaS$_3$ showing the differences between the temperatures calculated from conduction-dominated and convection-dominated models of heat dissipation.
mm wide and 4.09 mm long. The effective spring constant of this system was 500 N/m. The room temperature mechanical bias was 40 microns. In this case the CDW phase transition was severely depressed to 193.5 (+/- .5) K corresponding to a uniaxial strain of 5.1 (+/- .1) x 10^-3. The overall dilation of the sample was in the range of 3 microns which could conceivably reduce the strain by 8% during a single trial.

5.6.3 Organization of Results

The thermal expansion results for o-TaS$_3$ turn out to be very complicated. There is a significant variation from sample to sample which may be a result of strain differences or an expression of the sample dependant effects often associated with these materials [5.12]. The presence of very large electric fields in the vicinity of the CDW phase transition, particularly when cooling, may play a large role in complicating the dilation results [5.13]. For the purpose of simplifying the description and discussion the observations are divided into the three categories listed below.

The divisions used here are based upon observations made on the .18% or medium strain sample. For this sample it was found that a division based on the trial's starting temperature, $T_s$, was appropriate. It will be recalled from the discussion above that the starting temperature is the lowest temperature that the sample attains immediately prior to the commencement of an experimental trial.
The use of starting temperature may be easily motivated. In the first place this temperature will bear directly on the particular thermodynamic phase that the sample enters or leaves as it is warmed and then cooled. Furthermore, in the case of these "self-heated" expansions the starting temperature is directly related to the magnitude of the electric field that the sample experiences while undergoing its CDW phase transition. Generally, the higher the starting temperature the lower this electric field will be at $T_c$.

The divisions used here attempt to separate three effects through the starting temperature. The first category attempts to examine the CDW phase transition with the least attendant electric field effects. For this reason trials with starting temperatures close to $T_c$ are chosen in order to reduce as far a possible the electric fields at the transition.

The second category examines the behaviour of the sample for all those trials that have starting temperature below 163 K. This is because the presence of anomalies in the dilation of the .18 % strain sample suggest that there may be a phase transition near 163 K.

In the final category the dilation is examined for starting temperatures above 163 K. Again in the .18 % strain results it is found that an unusual dilation discontinuity is superimposed on the CDW phase transition for trials that begin between 163 and 173 K. By confining the observations to starting temperatures above 163 K it is hoped that the effects of the lower anomaly in the second category may be minimized.
5.6.4 Examination of the CDW phase transition

In order to minimize the effects of the large DC electric fields present in these experiments near the CDW phase transition the starting temperature is brought as close to $T_c$ as is practical. There is an effective minimum difference between these two temperatures which arises from the difficulty in identifying the transition in the resistance signal.

In the case of .09 % strain the best results are obtained at a starting temperature of 192 K. The associated electric field at the 215 K phase transition was then 4.91 V/cm. For the sample experiencing a strain of .18 % the closest starting temperature was found at 183.5 K. This leads to an electric field of 4.74 V/cm at the 210.5 K phase transition. Finally, the .51 % strain sample was brought to a starting temperature of 174.9 K. The electric field near the CDW phase transition at 193.5 K was then 4.23 V/cm.

These three results are shown in figure 5.22. The low and medium strain dilation signals possess clear slope discontinuities at their respective phase transitions. There is also such a discontinuity in the high strain result but it is too small to be seen on this scale.

In order to examine the region of the phase transition more closely a linear background expansion is removed from each curve as may be seen in figure 5.23. For the .09 % and .18 % strain samples the background removed was 6 ppm/K. In the case of the .51 % strain sample the removed background was 4.3 ppm/K.
The shape of these dilation results allows the primary conclusion to be drawn out. Generally, in the absence of strong ambient electric fields the CDW phase transition in o-TaS$_3$ is expressed as a simple negative slope discontinuity characteristic of a second order phase transition.

The magnitude of this discontinuity in the slope is, however, a widely varying quantity. In Table 5.1 may be found a series of estimates of the thermal expansion for these results based on a conduction-dominated model of the heat dissipation. Table 5.2 repeats these estimations based on a convection-dominated model of the heat dissipation. It is expected that the true figures for this transition will be some sort of weighted average of the two.
Figure 5.22 Absolute dilation for o-TaS$_3$ as a function of temperature. Results for three different uniaxial strains.
Figure 5.23 Dilation of $\alpha$-TaS$_3$ with constant linear backgrounds removed. Results for three uniaxial strains.
Table 5.1 Thermal expansion near the CDW phase transition

Estimates based on the conduction-dominated model of heat dissipation. All thermal expansion figures accurate to within 0.3 ppm/K.

<table>
<thead>
<tr>
<th>strain</th>
<th>$\alpha$ (T&lt;T$_C$)</th>
<th>$\alpha$ (T&gt;T$_C$)</th>
<th>$\Delta\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.09%</td>
<td>7.7 ppm/K</td>
<td>5.8 ppm/K</td>
<td>-0.9 ppm/K</td>
</tr>
<tr>
<td>.18%</td>
<td>7.1 ppm/K</td>
<td>5.7 ppm/K</td>
<td>-1.4 ppm/K</td>
</tr>
<tr>
<td>.51%</td>
<td>4.4 ppm/K</td>
<td>4.0 ppm/K</td>
<td>-0.4 ppm/K</td>
</tr>
</tbody>
</table>

Table 5.2 Thermal expansion near the CDW phase transition

Estimates based on the convection-dominated model of heat dissipation

All thermal expansion figures accurate to within 0.3 ppm/K.

<table>
<thead>
<tr>
<th>strain</th>
<th>$\alpha$ (T&lt;T$_C$)</th>
<th>$\alpha$ (T&gt;T$_C$)</th>
<th>$\Delta\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.09%</td>
<td>6.4 ppm/K</td>
<td>4.9 ppm/K</td>
<td>-1.5 ppm/K</td>
</tr>
<tr>
<td>.18%</td>
<td>7.0 ppm/K</td>
<td>5.1 ppm/K</td>
<td>-1.9 ppm/K</td>
</tr>
<tr>
<td>.51%</td>
<td>4.3 ppm/K</td>
<td>3.7 ppm/K</td>
<td>-0.6 ppm/K</td>
</tr>
</tbody>
</table>

The wide variation of thermal expansion coefficients is difficult to explain in any quantitative manner. The reasons for these differences may lie in the differing strain values or residual effects of the electric fields. They may also be due sample-dependant effects which arise from the sample's sensitivity to local
impurities or to differences in the handling of the samples. Having said this, it is felt here that the thermal expansion of the 0.51 \% strain sample owes the bulk of its reduction from the lower strain expansion values to the high value of its strain. Various other experiments which examine the dynamical properties of o-TaS$_3$ find that there is a "critical" strain between 0.4 \% and 0.5 \% [5.9, 5.23].

Finally, in figure 5.24 the variation of the coefficient of thermal expansion is shown as a function of temperature. The sharp discontinuities present in the thermal expansion at the CDW phase transition are clearly resolved in these curves for all three strain values.

5.6.5 Dilation results: starting temperatures below 163 K

The reason for confining this examination to results gathered for starting temperatures below 163 K will become clear in this section. Figure 5.25 shows three representative results for the three strain values employed here. For the 0.09 \% strain a small bump in the dilation may be found near 160 K, well below the phase transition at 215 K. In the case of the 0.18 \% strain sample there is a dramatic anomaly near 160 K still well below the CDW phase transition at 210.5 K. The dilation results for the 0.51 \% strain sample show no evidence for such a dilational anomaly below $T_c$. The reason for these low temperature anomalies is not understood.

The relative dilation results in figure 5.26 illustrate the nature and evolution of
Figure 5.24 Absolute thermal expansion of o-TaS$_3$ as a function of temperature.

Three different uniaxial strains.
Figure 5.25 Dilation of $\alpha$-TaS$_3$ for trials that begin below 163 K. Results for three different uniaxial strains shown.
this anomaly in the case of the .18 % strain sample. Here, a constant thermal expansion of 5 ppm/K is removed from each of these dilation results. The curves are shown for a series of successive trials with starting temperatures ranging from 141 K to 161 K.

It is first noted that as the starting temperature rises the strength of the anomaly is gradually reduced. When the starting temperature rises above 163 K the anomaly has completely disappeared. A tentative conclusion would be that the anomaly in the dilation expresses the existence of a new thermodynamic state which has an onset temperature of 163 K.

A second observation is that the temperature position of the anomaly is not fixed. As the starting temperature rises so too does the bump in the dilation signal. Thus, it is likely that the temperature position of the anomaly does not contain information crucial to the onset of this state. If the position of the anomaly is not fixed in temperature it may be fixed in the electric field. Figure 5.27 shows the variation of the anomaly position ("peak" position) in temperature and in electric field as a function of starting temperature. It is apparent that the anomaly is roughly fixed in electric field at 4.2 V/cm to within 10 %. This characteristic may hold some clue to the origin of this anomaly.

Finally, the presence of this anomaly affects the second-order phase transition in this material. When the dilation anomaly is strong the CDW phase transition is rounded and spread out. As the bump is reduced in magnitude the phase transition becomes sharper. Table 5.3 gives the results of an average of thermal
Figure 5.26 Relative dilation of o-TaS$_3$ with a uniaxial strain of 0.18%. A background of 5 ppm/K has been subtracted from each. All trials begin below 163 K.
Figure 5.27 Temperature position and electric field position of lower anomaly in \( \alpha\)-TaS\(_3\) as a function of starting temperature.
expansion coefficients near the phase transition estimated for the conduction-dominated dissipation model. Table 5.4 repeats this analysis under the convection-dominated model.

Table 5.3 Thermal expansion near CDW transition: $T_s < 163$ K
Estimates based on the conduction-dominated model of heat dissipation.
All thermal expansion figures accurate to within 0.3 ppm/K.

<table>
<thead>
<tr>
<th>strain</th>
<th>$\alpha (T&lt;T_C)$</th>
<th>$\alpha (T&gt;T_C)$</th>
<th>$\Delta \alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.09 %</td>
<td>6.8 ppm/K</td>
<td>6.0 ppm/K</td>
<td>- 0.8 ppm/K</td>
</tr>
<tr>
<td>.18 %</td>
<td>5.9 ppm/K</td>
<td>3.9 ppm/K</td>
<td>- 2.0 ppm/K</td>
</tr>
</tbody>
</table>

Table 5.4 Thermal expansion near CDW transition: $T < 163$ K
Estimates based on the convection-dominated model of heat dissipation.
All thermal expansion figures accurate to within 0.3 ppm/K.

<table>
<thead>
<tr>
<th>strain</th>
<th>$\alpha (T&lt;T_C)$</th>
<th>$\alpha (T&gt;T_C)$</th>
<th>$\Delta \alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.09 %</td>
<td>6.3 ppm/K</td>
<td>4.9 ppm/K</td>
<td>- 1.4 ppm/K</td>
</tr>
<tr>
<td>.18 %</td>
<td>5.4 ppm/K</td>
<td>3.4 ppm/K</td>
<td>- 2.0 ppm/K</td>
</tr>
</tbody>
</table>

It is seen that although the low temperature anomaly seems to round out the
phase transition on average the usual behaviour is recovered. The exception to this is the .18 % strain experiment under the conduction-dominated model. Here, the discontinuity is roughly 30 % larger than that measured when $T_s$ is near $T_C$ (section 5.6.4). The reason for this is not known but an unusual dilation signal is observed in the .18 % strain sample which may account for this. This third and final anomaly is the subject of the following section.

5.6.6 Anomalous results near CDW transition for $T_s > 163$ K

In figure 5.28 may be found a series of dilation results gathered from the .18 % strain sample for starting temperatures above 163 K. In this way it is hoped that the attendant effects due to the low temperature anomaly treated in section 5.6.5 are minimized. The anomaly may be seen as an increase in the effective slope discontinuity about the phase transition at 210.5 K. In addition, the anomaly also seems to broaden the CDW phase transition. These results are not present in the low or high strain samples.

The behaviour of this anomaly may be more readily appreciated if a constant background thermal expansion is subtracted from the data. In figure 5.29 such a background of 5 ppm/K is subtracted from the data. As may be seen the anomaly rounds and broadens the transition both above and below $T_C$. The effect of the anomaly is to decrease the slope of the dilation above the phase transition which has the effect of increasing the discontinuity in the thermal expansion at the CDW
Figure 5.28  Dilation of $\alpha$-TaS$_3$ under a strain of .18 %. All trials begin between 163 and 173 K.
phase transition. This is thought to be the reason for the high value of the discontinuity in the thermal expansion found in Table 5.3 for the .18 % strain sample.

As the starting temperature rises the strength of this anomaly decreases until for $T_s = 173$ it has disappeared altogether.

The exact nature of this anomaly can only be guessed at but it is possible to bring out some crucial features. By assuming the uppermost curve in figure 5.29 represents the "ordinary" behaviour this curve may be subtracted from the upper results to determine what sort of behaviour is superimposed on the CDW phase transition. This is done in figure 5.30. The anomaly now reveals itself as a dilation (rather than expansion) discontinuity which begins near 200 K and stretches out in a broad curve to temperatures well above the CDW phase transition. The initial size of this discontinuity is 25 ppm but as the starting temperature rises from 163 K to 173 K this gradually diminishes to zero. It is interesting to note that the onset of this anomaly in the dilation signal may be correlated to a small discontinuity in the negative logarithmic derivative of resistance with respect to temperature at 200 K. The anomaly may be viewed in slightly different form in figure 5.19 near a power of 1.7 watts. This suggests that these observations are a result of the internal constitution of the sample rather than instrumental effects.
Figure 5.29 Relative dilation of o-TaS$_3$ under a strain of .18 %. A background of 5 ppm/K has been removed. All trials begin between 163 and 173 K.
5.7 Discussion of the o-TaS$_3$ results

The discussion of these dilation results for o-TaS$_3$ begins with the CDW phase transition. It has been found that the CDW phase transition in these samples results in a negative discontinuity in the coefficient of thermal expansion.

The variation in the coefficient of thermal expansion between the .09 % strain sample and the .18 % strain sample might be expected from the usual sample-dependant effects that are legion in these materials. On the other hand, the effect of the strain is divided between the normal state and the CDW state thermal expansions just as it is in the .51 % strain sample. This may point to a strain dependant effect which saturates at high values of strain. The strain of .51 % is well in excess of the typical critical strains that are often quoted for this material on the basis of resistive hysteresis anomalies [5.9]. In order to ascertain the origin of these effects many, systematic, strain experiments must be attempted on this material.

The sign of the change in the thermal expansion is negative and so contradicts the predictions made by M.R. Hauser et al. on the basis of their simple, one-dimensional anharmonic model [5.11]. However, o-TaS$_3$ may not be an ideal candidate for the application of this model. In the first place, the anharmonic model completely ignores the contribution of fluctuations in this system. In the case of NbSe$_3$ the system is not as one-dimensional as its overall appearance might suggest and as such fluctuations may be discouraged [5.14]. o-TaS$_3$ is quite
Figure 5.30 Dilation of o-TaS$_3$ with the presumed "ordinary" dilation near $T_c$ subtracted. $163 \text{ K} < T_s < 173 \text{ K}$. 
one-dimensional with fluctuations contributing to the formation of a pseudo-gap well above $T_c$ [5.12]. Thus, the fluctuation component may be too large to be ignored in $\alpha$-TaS$_3$. Perhaps more importantly, the periodic lattice distortion (PLD) in $\alpha$-TaS$_3$ is not confined to the chain direction as it is in NbSe$_3$. The reduced wavevector for this system in its CDW state is $q_{CDW} = (0.5, 0.125, 0.5)$ which implies a considerable out-of-chain motion on the part of the atoms of the unit cell [5.12]. Thus, the CDW in $\alpha$-TaS$_3$ is manifestly three-dimensional and it is not surprising that the one-dimensional anharmonic model fails to apply.

If the phase transition in $\alpha$-TaS$_3$ is truly second order then the Ehrenfest relations predict changes in the specific heat and elastic modulus at $T_c$. The prediction for $\Delta C_p$ are made very uncertain by its dependence on the absolute magnitude of the Young’s modulus for this material. The figure measured by Brill is 350 (+/-50) GPa [5.15] while Tritt et al. find 100 (+/-1) GPa [5.16]. With the variation in the thermal expansion discontinuity folded in the calculations it is found that the specific heat should possess a discontinuity somewhere between -34 kJ/m$^3$-K and -3.8 kJ/m$^3$-K at the CDW phase transition. There are no measurements of the specific heat of $\alpha$-TaS$_3$ in the region of the phase transition with which to compare these calculations.

The relative change in the Young’s modulus at the phase transition is not dependant on the absolute magnitude of the elastic modulus. In the case of a thermal expansion discontinuity of -0.9 ppm/K the associated fractional modulus change would be 0.43 (+/-0.05) %. For the higher figure of -2.4 ppm/K this rises to
1.3 (+/-0.1) %. These figures may be compared to those changes estimated from
the vibrating-reed experiments of Brill [5.15]. Brill's estimates are in the range of
-2 % for \( \Delta Y/Y \). Although the magnitude is comparable the sign is in serious error.
It should be noted that these changes in the elastic modulus would be easily seen
in the dilation experiments discussed in this chapter. No dilational anomalies may
be unambiguously separated from the results for strains of 0.09 % and 0.51 %.
However, the 0.18 % strain sample does display an unusual dilation anomaly in the
vicinity of the CDW phase transition which may be separated from the "ordinary"
dilation. In this case, shown in figure 5.30, there is an unexplained anomaly in the
dilation which varies in magnitude with the starting temperature of the individual
trail. The shape need not be of concern here as the elastic "discontinuities"
measured in these materials are almost never true discontinuities [5.15]. Taking
the uppermost curve, the anomaly is approximately -25 ppm (considering a
change from low to higher temperature). The shrinkage of the sample might
suggest that it is seeking a new equilibrium that can support more stress: that is,
its modulus has increased. This would correspond to an increase in the Young's
modulus of +1.4 %, remarkably close to one of the predicted values above. A
softening, as measured by Brill, is not at all supported by this data. However
successful this interpretation might be it still begs the question of what happens to
the presumed modulus change as the starting temperature rises. Clearly, the
change disappears but the discontinuity in the thermal expansion merely becomes
more easily resolved. This may be associated with the large electric fields in the
system which may either affect the modulus directly or prepare the system in a special state [5.13]. Measurements of the specific heat would go a long way to resolving the contradictions raised by the Ehrenfest relations in this material.

The anomalies found in the dilation below $T_c$ present an interesting if complex picture of o-TaS$_3$ in combined electric and strain fields. In the first place it is noted that the anomalies are quite strong in the .18 % strain sample and are present in a much weaker form in the .09 % strain sample. No anomalies in this range of temperature are observed at all in the .51 % strain sample. The discovery of anomalies in two different samples lend credence to the assertion that these are intrinsic to the CDW rather than spurious instrumental effects. Again, the strength of the anomalies may be due to the varying strain or sample-dependant effects.

The second important observation is that the anomaly vanishes when $T_s$ is raised above 163 K. This would strongly imply that some kind of transition occurs between 160 and 163 K in this system (the uncertainty is due to the spacing of individual trials). A second CDW phase transition has been postulated for this material. Scattering experiments suggest that the incommensurate CDW state smoothly changes to a commensurate CDW below approximately 150 K [5.17]. In experiments designed to measure the modulus softening above the threshold electric field it was found that the magnitude of the softening increased dramatically when the temperature was lowered to 160 K [5.18].

This might be the point to suggest a possible origin for these dilational effects...
which is consistent with the scattering and modulus experiments mentioned above. This suggestion depends upon the association of CDW phase solitons, electric fields and metastable states in o-TaS$_3$. There are numerous transport experiments which suggest the internal CDW arrangement within o-TaS$_3$ is dominated by and expressed as metastable states. Metastable states are suggested in the remnant polarization experiments of Brown et al. [5.19]. Direct observation is reported in the X-ray diffraction measurements of Tamegai et al. [5.20]. Solitons are the favoured interpretation of the studies of the optical properties of o-TaS$_3$ [5.21].

In their paper on electric field-induced disorder in K$_{0.3}$MnO$_3$ (blue bronze) Fleming et al. draw a connexion between the CDW phase soliton lattice and the metastable states in that system [5.22]. These authors measure a dramatic transverse disorder in their X-ray measurements when blue bronze is cooled in an electric field below the temperature where the CDW is expected to be commensurrate. This may be compared to the "frozen" polarization which is present in the field-cooled samples of the same system [5.13]. The polarization is explained in terms of local displacements of the CDW. If the pinning sites are allowed to vary spatially then it is entirely possible that some regions of the CDW move under the influence of the electric field before others do. This would lead to a loss of transverse phase coherence while the motion simultaneously builds up a macroscopic dipole moment. The situation encountered in the commensurate CDW state is one in which the moving objects are the widely spaced CDW phase solitons that characterize the commensurate state. These are arranged in sheets
perpendicular to the chain axis. When an electric field is applied they "bow" outwards. This produces a local motion of the CDW which is metastable: when the electric field is removed the local regions do not relax. The number of metastable states is then closely related to the number of impurity pinning sites.

All the dilation experiments reported here are "field-cooled" in the sense that the electric field is only gradually reduced when bringing the sample back to the probe temperature. Thus, it is reasonable to suppose that these fields result in a "frozen-in" distortion of some CDW object in the sample. It is significant that the anomalous dilation vanishes when the sample is no longer cooled below 160 K. This is near the temperature where the scattering experiments suggest that the CDW state undergoing a C/I transition [5.17]. This would suggest that the CDW objects that play the most important role in these effects are the set of widely spaced CDW phase solitons found in the commensurate CDW state. The distortion of these phase solitons is the origin of the metastable states in this material. It has been shown that the application of a uniaxial strain in excess of 0.4 % can drive the CDW in \(\alpha\)-TaS\(_3\) into a single stable state [5.23]. It is therefore not surprising to observe that the anomalous dilation seen for strains of .09 % and .18 % disappears when the strain is increased to .51 %. In the latter case the electric field has essentially no effect on a system which no longer possesses any metastable states.

The correlation of these metastable states to anomalies in the modulus of elasticity is not difficult under the aegis of the prevailing theoretical models (q.v.)
chapter six). For example, there is a sudden drop in the elastic softening at threshold as the temperature is caused to rise above 160 K in o-TaS$_3$ [5.18]. Within the phase relaxation model [5.24] this would imply that there is a sudden change in the distribution of characteristic relaxation times for the metastable states of the CDW. If the metastable states originate within the phase solitons then a shift from a commensurate CDW to an incommensurate CDW would certainly lead to different set of relaxation times. Perhaps these might arise when the phase solitons become close enough to interact. Another example is the reduction of the shear modulus softening at threshold when the strain is raised above .5 % [5.25]. This would certainly follow from the preceding arguments since the high strain wipes out the metastable states that the phase relaxation model requires.

The reason why a postulated "frozen-in" distortion of the phase solitons in the CDW would result in a dilation anomaly is a matter of still further speculation. Domain wall motion caused by external magnetic, electric or stress fields will profoundly affect the thermal expansion of a variety of compounds [5.26]. The production of an electrically ordered CDW state in o-TaS$_3$ would naturally lead to changes in the lattice modes of such a closely interacting electron-phonon system. The precise mechanism is certainly worthy of further study.
Chapter Six  Threshold Field Effects

6.1 Introduction

The phenomena of non-ohmic effects above the threshold electric field has been mentioned in the chapter on materials. The description of the physics of the "sliding" CDW state in the quasi-one-dimensional CDW compounds continues to be a source of great controversy in the field. In addition to the well-documented electrical response to fields in excess of threshold there are also striking elastic anomalies which accompany the onset of non-ohmic conduction [6.1, 6.2]. The explanation of this facet of the CDW system’s behaviour may provide an alternate route to a theoretical description. Certainly, any theory proposed must treat the elastic response as a function of electric field.

The techniques used to examine the longitudinal Young’s modulus of the quasi-one-dimensional compounds have generally followed two lines. A brief description of these two types of experiments is germane to the discussion that follows. The first is the Barmatz vibrating-reed technique [6.3]. Here the sample is caused to undergo longitudinal flexions at its natural resonant frequency. The resonant frequency may then be simply related to the Young’s modulus. Using a phase-locked-loop method the resonant frequency of the sample is tracked as a function of a DC electrical bias providing a very sensitive gauge of the relative changes of
the Young's modulus and internal friction near the threshold field. The vibrating-reed technique covers a mechanical frequency range between 100 Hz and 1 MHz.

The second technique is an ultrasonic velocity experiment in which the sound velocity for longitudinal vibrations is measured as a function of the applied electric field [6.4]. This technique typically operates at a frequency near 10 MHz.

For investigations carried out on o-TaS$_3$ the behaviour of the longitudinal elastic properties may be quickly summarized [6.5]. In the case of negligible Joule heating effects the modulus and internal friction remain unchanged for electric fields below threshold. At and above threshold the modulus decreases in concert with the differential resistance while the internal friction rises. The magnitude of the "softening" of the system is found to decrease as the mechanical frequency of vibrations increases. Often this decrease may be described by a power law, $w^P$ where $w$ is the frequency of mechanical vibrations and $P$ lies between 0.5 and 0.75.

These results present interesting opportunities for the construction of theoretical models of the CDW sliding state. However, advancement is somewhat hampered by the low-frequency limit of the two experimental techniques outlined above. It seems clear that the frequency domain of greatest interest will lie between 0 and 100 Hz. This follows from the power law behaviour of the frequency response: the magnitude of the modulus changes must either saturate at low frequencies or go through some maximum. Naturally, the magnitude cannot be allowed to diverge. Following Mozurkewich [6.6] the various competing theoretical models may be divided into two broad categories.
In the first category are theories which suppose that the "stationary" CDW state is inherently different from the "sliding" CDW state. The reasons advanced for this difference are varied. One case is the semi-classical model in which the lattice and CDW are each represented by a series of "balls" and "springs". Pinning sites in the lattice allow the two to be coupled below the threshold field. When the electric field rises above threshold then the CDW "slides" averaging out the pinning potentials and allowing the CDW and lattice to become decoupled. This leads to a decrease in the elastic modulus by an amount roughly equal to the CDW spring constant [6.1]. In another model the CDW and lattice are coupled together by an electron-phonon interaction. It is then supposed that the "sliding" CDW state modifies the ability of the CDW to screen acoustic phonons. This leads again to a reduction in the longitudinal elastic modulus [6.7].

The second category of explanation draws on the ideas of Brill and Roark [6.8] and attributes the changes in the elastic modulus to the relaxation of some kind of "defect" in the CDW. In the stationary CDW state this relaxation time is long and consequently the system appears stiff to elastic demands. When the CDW "slides" the relaxation time is drastically reduced. Now the system can respond to elastic demands more quickly and so appear "softer".

The second category has a distinct advantage over the first in that a frequency-dependant response of the magnitude of modulus change is naturally incorporated into the model. The first category does not allow for such behaviour unless it is inserted "ad hoc" into the theory. However, this cannot in itself determine the
validity of either set of models.

Recent experiments have re-kindled interest in the elastic properties of the quasi-one-dimensional CDW compounds. Tritt and co-workers have managed to measure the Young's modulus of o-TaS$_3$ at elastic frequencies below 0.1 Hz [6.9]. Their technique is a modification of a capacitive dilatometric apparatus with the sample subject to constant loading. The remarkable result that they report is that to within the noise level of the experiment, 0.2%, there is no softening of the Young's modulus for electric fields up to 3 times threshold. Thus, for o-TaS$_3$, one is led to expect that the frequency response of the Young's modulus changes goes through some kind of maximum between 0.1 Hz and 100 Hz.

The experiments detailed in this chapter are able to measure the changes in the Young's modulus in the zero-frequency or static limit. The sample is mounted in the cantilever mode (q.v. chapter 3) which places a uniaxial stress on the sample by means of the cantilever arm. As the electric field is swept in the region of threshold the position of the lever is carefully monitored in order to detect any dilational shift in the sample. A measured dilation of the sample may have three sources. In the first place there may be those changes in the crystalline structure ordinarily due to heating effects, in this case driven by the sample's Joule heating. Secondly, there may be changes due to the strong electric fields applied to the sample. Finally, any alteration in the longitudinal elastic modulus will be translated into a dilation change with the sample mounted in the cantilever configuration. Assuming for the moment that these effects may be separated, the
change in the Young's modulus and the elastic component of the dilation signal are related by,

\[
\frac{\Delta Y}{Y} = \frac{\Delta L}{L} + \frac{\eta}{Y}
\]  \hspace{1cm} (1)

where \( Y \) is the Young's modulus, \( \Delta L/L \) is the detected change in the dilation signal and \( \eta \) is the uniaxial stress on the sample. The estimate of the latter quantity is very difficult owing to the uncertainty in the sample cross-section and the temperature dependences of the elastic constants of the cantilever. However, a different approach may be taken. The strain dependence of the CDW phase transition for both \( \alpha \)-TaS\(_3\) and NbSe\(_3\) have been measured by R.S. Lear \textit{et al.} [6.18]. If the depression of the CDW phase transition for a particular cantilever configuration is known then the changes in the Young's modulus may be estimated from,

\[
\frac{\Delta Y}{Y} = \frac{\Delta L}{L} + \frac{\Delta T_C}{d T_C / d e}
\]  \hspace{1cm} (2)

where \( d T_C / d e \) is the uniaxial strain derivative of the CDW transition temperature. In this way the estimates of relative changes in the Young's modulus are freed from the uncertainty in the absolute magnitude of the Young's modulus which may be considerable.
6.2 Experiments on o-TaS$_3$

The experiments performed here were almost identical to the single 'trials' described in the chapter on Active dilatometry. After the usual preparation sequence (sample mounting, contact mounting etc.) the samples were cooled to 77 K and tunnelling initiated. In this case no external heater was used in order to maintain the greatest amount of thermal stability during the experiments. The drift rate of the probe fell in this case to 1 K/hr.

As before the sequence of events comprising a single 'trial' were repeated here. There are only two exceptions to the description in chapter five. First, the experimenter, not the computer, initiated a 'trial'. This was done to allow certain manipulations of the tunnelling parameters to optimize the dilatometric sensitivity of the probe. These manipulations amounted to the rather haphazard changing of the tunnelling current, bias voltage and feedback time constant to arrive at the quietest tunnelling possible. The second exception was that in some cases the 'second derivative' was substituted for the differential resistance in the measurement rota. The 'second derivative' is in actual fact the local curvature of the I/V curve measured by a lock-in amplifier operating in the '2f' mode. It can be a more sensitive measure of the onset of non-linear conduction in cases where heating effects may interfere with the positioning of the threshold field by 'rounding' the differential resistance signal.

Three experiments form the basis of this section on o-TaS$_3$. These were undertaken at widely differing uniaxial strains in order to identify any strain-
dependant effects associated with the elastic modulus softening near the threshold electric field. It is known, for example, that a uniaxial strain in excess of 0.5% will reduce the softening of the shear modulus from 20% to zero in o-TaS$_3$ [6.20]. Consequently, it is prudent to keep this figure in mind when reviewing the experimental results presented here.

All samples used in these experiments were culled from that same growth lot that supplied samples for the active dilatometry chapter. As mentioned in the materials chapter this growth lot is characterized by a zero-strain transition temperature of 219.75 K. It also has an unusually low threshold electric field, typically between 100 and 150 mV/cm well below $T_c$. In the following discussion the three experiments are examined in turn for any Young’s modulus effects near the threshold electric field. In all cases no softening was detected within the noise allowed by the dilation signal and the depression of the transition temperature (as seen in equation 2).

(a) Low Strain Results

The o-TaS$_3$ sample used here was extracted from lot # 1354 and was 6.28 (+/- .01) mm long. The lever was fashioned from a loop of 0.004" molybdenum wire. Such cantilevers generally lead to low uniaxial strains. In figure 6.1 the position of the phase transition is identified as the peak in the negative logarithmic derivative of resistance with respect to temperature. The phase transition found at 215.0
($+/-.25$)K leads to a depression of $4.75$ ($+/-.25$) K in $T_C$.

The stress dependence of the CDW phase transition has been measured by R.S.Lear et al. and found to be $15$ ($+/1$) K/GPa [6.18]. In fact, these authors measure the strain dependence of this transition and then divide this figure by the Young's modulus as measured by Brill of $350$ ($+/50$) GPa [6.19]. Thus, the strain dependence may be calculated as $5250$ ($+/75$) K. The error estimate is based on the Lear et al figure which obviously cannot include the uncertainty in Brill's measurement of the Young's modulus. Consequently, the strain experienced by the sample in this case is $0.090$ ($+/0.006$) %. It is not possible to estimate the uniaxial stress from the mechanical bias since the cross-section of the sample is less than the minimum resolution of the travelling microscope used for these measurements, 10 microns. When compared to the critical strain found by Xu and Brill [6.20] of 0.5 % this figure may be deemed "low".

In figures 6.2 and 6.3 the results of a simultaneous measurement of the dilation and differential resistance as a function of electric field are shown for 148.6 and 152.1 K respectively. The threshold field is estimated between 250 and 300 mV/cm which is somewhat larger than typically expected. It is possible that the low resistance of this sample leads to rather more Joule heating than in other experiments. At 1 V/cm the dissipated power is already 10 milliwatts. Thus, the differential resistance signal could be "rounded" and so prevent a more precise determination of the threshold field for this sample.

In the dilation signal there is no effect in the vicinity of the threshold electric
Figure 6.1 Logarithmic derivative of resistance with respect to temperature for o-TaS$_3$. The CDW transition at 215.0 K indicates a uniaxial strain of .09 %.
field beyond what might be expected through Joule heating. The noise in this signal allows an estimation of the upper limit on possible changes in the Young's modulus through equation 2. In both experiments a noise level of approximately 2 ppm yields an upper limit of 0.22 (+/-0.02) % for ΔY/Y. This figure is entirely compatible with the value determined by Tritt et al. of 0.2 % for an elastic frequency below 0.1 Hz [6.9].

(b) Intermediate Strain Results

In this case the sample was extracted from the growth lot # 1354 and was 6.52 (+/-0.01) mm long. The cantilever was a phosphor-bronze strip which generally applies a much larger stress than the molybdenum wire levers. The depression of the CDW transition temperature is evident in figure 6.4 where it may be placed at 197.0 (+/-0.25) K. This leads to a uniaxial strain of 0.43 (+/-0.01) % which is approximately 20% lower than the critical strain quoted by Xu and Brill [6.20]. For this reason the strain is termed "intermediate".

In figures 6.5 and 6.6 the results of a simultaneous measurement of the dilation and differential resistance for a swept electric field may be seen for the temperatures of 162.5 and 171.2 K respectively. There is little to choose between these or any of the 40 or so experiments performed between 160 and 200 K.

It is first noted that the threshold electric field is between 120 and 130 mV/cm which is in accordance with previous estimations. The relatively high resistance of this sample results in a small quantity of dissipated heat in these experiments - less
Figure 6.2 Dilation and differential resistance of $\text{o-TaS}_3$ as a function of electric field near 148.6 K.
Figure 6.3  Dilation and differential resistance for o-TaS$_3$ as a function of electric field near 152.1 K
than 14 microwatts. It is estimated that this would lead to a temperature rise of less than 0.03 K (based on parameters derived in the Active Dilatometry chapter). As a consequence the threshold field is well-resolved.

The dilation signal is absolutely featureless to within a noise level of 0.11 ppm. The reversal of slope is consistent with a sample that is insensitive to the electric field sweep and the small amount of Joule heating generated (the experiment increases the electric field to 200 mV/cm and then decreases this back to zero). The sample merely drifts with the temperature in the dilatometer cell. The absence of any dilational anomaly near the threshold field obviates the need to discriminate between elastic, structural or thermal effects as noted above. The intrinsic noise in the dilation signal places an upper limit on each of these effects near the threshold field. The upper limit on changes in the Young's modulus in these experiments is \(2.5 \times 10^{-5}\). This is approximately 2 orders of magnitude lower than the figure measured by Tritt et al. [6.9]. However, it should be pointed out that the electric field in these experiments is only swept to twice threshold. In the experiments of Tritt and co-workers the electric field is allowed to increase to three times threshold in the search for elastic effects.

(c) High Strain Results

In the final o-TaS\(_3\) experiment a sample 7.32 (+/-0.01) mm long was drawn from the sample lot # 1354. The use of a phosphor-bronze lever led to a
Figure 6.4 Logarithmic derivative of resistance with respect to temperature for o-TaS$_3$. CDW transition at 197.0 K indicates a uniaxial strain of .43 %. 
Figure 6.5 Dilation and differential resistance for o-TaS$_3$ as a function of electric field near 162.5 K.
Figure 6.6 Dilation and differential resistance of o-TaS$_3$ as a function of electric field near 171.2 K.
depression of the CDW phase transition to 182.8 K as may be seen in figure 6.7. This would imply a uniaxial strain of 0.70 (+/-0.05) %. This is 40% higher than the critical strain measured by Xu and Brill [6.20] and so is given to be "high".

In figure 6.8 the dilation and the differential resistance are shown as a function of electric field at a temperature of 112.4 K. The threshold is evident at 100 mV/cm. The total power dissipated by the sample in this sweep is less than 30 microwatts which would indicate a temperature rise of less than 0.06 K.

The dilation is entirely unaffected by the electric field sweep and simply drifts with the dilatometer cell. The noise level of this signal is 0.35 ppm which places an upper limit of 5.0 (+/-0.3) x 10^{-5} on possible changes in the Young's modulus up to 3 times the threshold electric field.

In the second experiment, shown in figure 6.9, the differential resistance is replaced by the "2f" mode or curvature signal as mentioned above. Again, the threshold field is seen at 100 mV/cm. The noise in the dilation signal is somewhat improved and now lies at 0.15 ppm. This implies an upper limit of 2.1 (+/-0.1) x 10^{-5} for changes in \( \Delta Y/Y \). The large "dip" in the dilation signal is actually a calibration mark for the capacitance bridge : it corresponds to bringing the capacitance bridge 0.1 pF out of balance. Apart from the departure from zero in the "2f" mode signal there are also a series of peaks in this measurement. The reason for these is not understood but in the appendix it is suggested that these constitute evidence for an internal degree of freedom in the electrical properties of the CDW.
Figure 6.7 Logarithmic derivative of resistance with respect to temperature for o-TaS$_3$. CDW transition at 182 K indicates a uniaxial strain of .70 \%.
Thus, detection of changes in the Young's modulus in the vicinity of the threshold electric field is limited only by the sensitivity of the dilation measurement. No softening can be observed in the Young's modulus at zero elastic frequency for the following strain values.

Table 6.1 Maximum fractional modulus changes at threshold electric field in o-TaS₃

<table>
<thead>
<tr>
<th>uniaxial strain</th>
<th>ΔY/Y (maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0 (+/-1) x 10⁻⁴</td>
<td>2.2 (+/-2) x 10⁻³</td>
</tr>
<tr>
<td>4.3 (+/-1) x 10⁻³</td>
<td>2.5 (+/-2) x 10⁻⁵</td>
</tr>
<tr>
<td>7.0 (+/-2) x 10⁻³</td>
<td>2.1 (+/-1) x 10⁻⁵</td>
</tr>
</tbody>
</table>

These results are consistent with measurements obtained for elastic frequencies below 0.1 Hz [6.9]. They are in dramatic contrast to the 2 % softening seen in this material at an elastic frequency of 300 Hz [6.5].

6.3 Experiments on NbSe₃

Measurements similar to those performed on o-TaS₃ were repeated on a sample of NbSe₃. However, these experiments were performed quite early on when the importance of the dissipated power was not appreciated. Consequently, no
measurements were made of the DC current and the experiments are hampered by this deficiency. In addition, the low resistance and high threshold fields in the NbSe₃ samples mean that Joule heating becomes a problem in these results. The complications presented by the heating effects are so great as to render these experiments essentially inconclusive so far as threshold field effects are concerned.

The sample of NbSe₃ was culled from the Dalhousie-grown lot # 1018 and is the same as that found in the Active dilatometry chapter. It was 7.10 mm long with a cross-section of 200 microns by 200 microns. The lever was formed from a loop of molybdenum wire 100 microns in diameter and 4.09 mm long, with a room temperature bias of .45 mm the uniaxial stress was nominally 50 MPa. The uniaxial strain in the temperature region of interest was deduced from the depression of the transition temperature. The reduction of the transition temperature by 0.3 K implies a uniaxial stress at 144 K of 80 MPa.

Experiments were performed at three different temperatures, 87 K, 120 K and 150 K. The latter temperature was well above the phase transition and was undertaken in order to make certain that the effects observed were due to the CDW alone.

As mentioned above the low resistance of NbSe₃ leads to heating effects which can complicate the interpretation of data. It is usual to employ the 'pulsed field' technique when heating effects are encountered in these CDW systems [6.10]. With the pulsed field the electric field is allowed to rise to very high values for short durations thereby restricting the quantity of integrated power dissipated by
Figure 6.8 Dilation and differential resistance for $\alpha$-TaS$_3$ as a function of electric field near 112 K.
Figure 6.9 Dilation and "2f" mode local curvature measurement of the I/V response for o-TaS$_3$ near 171.2 K.
the sample. Unfortunately, this scheme cannot be applied to the tunnelling dilatometer since the feedback electronics responsible for dilation measurement are too sluggish to follow the pulse frequency. A continuous wave experiment is the only avenue left to the tunnelling dilatometer. Shown in figure 6.10 is the differential resistance as a function of electric field for NbSe$_3$ at a nominal temperature of 87 K. It is apparent that the sample begins to heat as soon as the electric field rises from zero. The shape of the resistance rise is consistent with Joule heating within the sample. The first anomaly near 600 mV/cm is interpreted here as the onset of non-linear conduction. The second anomaly at 1.57 V/cm is believed to be the position of the phase transition. This second anomaly is in many ways similar to those observed in o-TaS$_3$ near the phase transition as found in the Active dilatometry chapter. Similar results were obtained at 120 K. The identification of the 1.57 V/cm anomaly in the dilation with the phase transition is strengthened by the observation that this anomaly disappears when the experiments are begun above the CDW phase transition as was the case at 150 K.

The associated dilation signal does not show any marked anomaly near the threshold electric field apart from the strong Joule-heating component evident in the figure. The search for a modulus softening for this material would reveal itself in these experiments as an increased dilation. This would then be superimposed on the thermally stimulated dilation. Clearly, a separation of these two effects cannot be made in an unambiguous fashion. The anomaly in the dilation at 1.57 V/cm is undoubtedly due to the CDW phase transition in this material. It may not
be associated with the threshold field effects. The interpretation of these experiments is, as pointed out above, plagued with difficulties. Chief among these is the co-mingling of elastic, structural and thermal effects in the single dilation measurement. The best efforts to improve this situation would first measure the dissipated power properly to allow a realistic subtraction of thermal effects. Next, a systematic programme of measurements with different uniaxial strains would allow the separation of structural from elastic effects. Based on the results of this analysis it is impossible to say whether or not there is a change in the elastic modulus at the threshold electric field at zero elastic frequency in NbSe$_3$.

6.4 Discussion

In the first place little may be concluded concerning the possible Young's modulus changes experienced by NbSe$_3$ at the onset of non-linear conduction. The results of the experiments on NbSe$_3$ are consequently set aside and attention is restricted to those observations made on o-TaS$_3$.

In order to explain the observed frequency dependence of the modulus changes in o-TaS$_3$ Brill and Roark have proposed a relaxation model [6.8]. The softening of the modulus at the threshold field is ascribed to the relaxation of an unspecified defect in the CDW. Within the model as originally cast there is a single relaxation time for the "stationary" CDW state, $t_F$, and another much shorter relaxation time for the "sliding" CDW state, $t_S$. If an experiment is so constructed as to measure
Figure 6.10 Dilation and differential resistance of NbSe$_3$ as a function of electric field near 87 K.
the elastic modulus on a time scale "t" then the result of that experiment will depend on how large "t" is with respect to \( t_r \) and \( t_s \). For example, if \( t_s < t < t_r \) then the CDW defect in the pinned state cannot relax on the time scale of the experiment. However, the defect can relax on this time scale when the CDW enters the "sliding" state. Consequently, the system appears more elastically responsive in the "sliding" state and a modulus reduction is observed.

The idea of a "sliding" CDW-assisted relaxation model has been extended by Mozurkewich who identifies the relaxing CDW "defect" as the CDW phase configuration [6.6]. This attempts to attain its optimum configuration in the presence of an externally applied stress by relaxation processes.

Mozurkewich begins with the Lee-Rice formulation of the CDW state which is a description suited to the weak-pinning limit [6.11]. In this limit the CDW is able to distort its local phase in an effort to minimize the sum of the pinning and distortion energies. The pinning sites are, of course, randomly distributed within the lattice and so yield a number of metastable phase configurations which are very nearly degenerate with the global minimum or optimal phase configuration. Each of these metastable phase configurations is separated from the optimal configuration by an activation barrier which is capable of trapping the CDW in a state with higher energy than the optimal phase configuration.

The specific energy of a metastable configuration will depend on the Lee-Rice energy which in its turn depends on the details of the band structure of the CDW system. An externally imposed stress field will modify the electronic overlap
integrals and so too the band structure. This leads to a shift in the energies of the metastable minima of CDW phase configurations. Thus, the CDW is motivated to alter its phase configuration in response to the application of an external stress. However, for the pinned CDW state this drive is resisted by the presence of activation barriers between the metastable and optimal configurations. Random, thermally driven "hops" are the only route to the minimum energy state but these will be slow on the time scale of a typical vibrating-reed modulus experiment. The CDW remains trapped in a phase configuration with an energy higher than the optimal state. The difference in energy between these two states will depend on the stress applied. If the energy difference depends quadratically on the stress then the entire system will appear more rigid.

The crucial assumption in Mozurkewich's description is that the optimal phase configuration may be more rapidly approached when the CDW enters its "sliding" state. It is believed that CDW motion takes place in a sequence of discrete "jumps" [6.12]. These "jumps" occur on a very short time scale and allow the CDW phase to re-configure more quickly when an external stress is imposed. Consequently, the CDW phase can attain its optimal configuration on the time-scale of the elastic modulus experiments and the entire system appears to "soften".

Mozurkewich points out that if the stress-dependent parameter is the CDW wavevector then two predictions will follow. First, the modulus reduction will be independent of the density of pinning sites in the host lattice. This has been shown in the case of o-TaS₃ for pinning sites created by electron irradiation [6.13].
The second prediction is that the temperature dependence of the modulus reduction will follow the square of the order parameter. This as well has been confirmed in o-TaS₃ [6.14].

The Mozurkewich phase relaxation model naturally incorporates the frequency dependence of the magnitude of modulus softening. However, if just a single relaxation time in the sliding state, \( t_s \), is assumed then the region of significant frequency dependence is confined to a small frequency region centred about \( f = 1/t_s \). On the other hand, a distribution of relaxation times in the "sliding" mode, \( g(t_s) \), can yield a power law dependence over many decades as is observed. The existence of "glass-like" distributions of relaxation times in these CDW systems has already been observed in measurements of the resistance and dielectric constants [6.15, 6.16, 6.17] and it is hardly surprising that such a distribution would arise from a phenomena whose origin lies in metastable states. Finally, the phase relaxation model predicts that the modulus reduction will tend to zero as the elastic frequency becomes much smaller than \( 1/t_s \).

The results obtained here would support the phase relaxation model of Mozurkewich. Physically, this model requires that the vibrating-reed and ultrasonic measurements lie in a frequency domain which is dominated by the "sliding" relaxation time distribution \( g(t_s) \). In the "stationary" CDW state the system is unable to relax on the time scale of the measurement since \( t_F \gg t \). When the threshold field is crossed then \( t_F \) is replaced by \( t_s < t \). The system is now able to relax and so appears "softer". In the case of the quasi-static limit the
"stationary" CDW will be given enough time to relax and respond to elastic demands. Crossing the threshold electric field might replace $t_f$ with $t_s$ but this has no effect on the final relaxed state of the system. Consequently, little or no modulus change is expected in this limit.

While this interpretation appears to be successful in the main, the final determination awaits experiments in the most interesting frequency region between 0.1 Hz and 100 Hz. In addition to supporting the conclusions of Tritt et al. [6.11], the results for $\alpha$-TaS$_3$ described in this chapter contribute a single yet crucial point to the frequency response of the modulus changes.
Chapter Seven Conclusions

7.1 Tunnelling dilatometer: problems and suggested improvements

It has been shown that the tunnelling dilatometer combines the moderate sensitivity of a capacitance dilatometer with the resolution engendered by a continuous measurement as a function of external fields. In this way it is clearly superior to the only other technique available for mechanically weak materials, X-ray diffraction. The best sensitivity that may be expected from the tunnelling dilatometer is approximately 5 Angstroms while the resolution in external fields is almost completely controlled by the experimenter.

When operated in its so-called "tip" mode, it is conceivable that the uniaxial stress placed on the sample during a dilatometric measurement may be reduced to negligible proportions. This would be considered an advance in so far as it permits the probing of structural phase transitions and the like without attendant experimental constraints. However, the tip mode makes other demands of conductivity and rigidity that can limit its application. Taken in sum, use of the tunnelling dilatometer on the more "conventional" solids may be of some value.

Dilation measurements on the truly mechanically weak solids can only be made in the cantilever mode. Therefore, it is impossible to reduce the uniaxial stress
placed on the sample to zero. Nevertheless, this particular mode does allow a systematic investigation of the strain-related effects on materials that are likely to be dominated by such interactions. With the proper amount of consideration it may be possible to devise a gallows-cantilever that allows the uniaxial strain to be modified in situ.

The greatest problem that faces the tunnelling dilatometer at the moment is the modification and maintenance of the local surface conditions where the electron tunnelling takes place. This would include the impurity layers that exist on the tip and surface as well as the local topography of the HOP graphite. The fluctuation of these conditions is the single greatest source of uncertainty in the dilation measurements and the reason why the experiments must be so often repeated. The difficulties encountered with the rough approach mechanism are certainly included under this general criticism.

In order to eliminate as many of these drawbacks as possible it is suggested here that the tunnelling feedback system be replaced with a laser-interferometric technique. The advantages counted by this alteration are manifold. In the first place, this modification would not substantially change the overall design of the probe. It may be recalled that the use of a feedback scheme to track sample position was adopted precisely because the dilatometer could then be insensitive to its details during operation. Samples would still continue to be mounted in the cantilever mode with the cleaved surface of the HOPG acting now as a mirror. A fibre-optic cable would bring the laser light to within a few tens of microns of the
HOPG surface. There its cleaved end and the HOPG surface would form an interference cavity. With spot sizes of the order of tens of microns and a cavity spacing of tens of microns the interferometric technique would clearly be insensitive to local surface conditions. This would allow restrictive pumping operations to be relaxed and improve the overall stability of the probe.

The use of an interferometer eliminates the necessity of an *in situ* approach mechanism and increases the overall dilation range of the probe far beyond the piezoelectric range (which can be profoundly limited at very low temperatures). This is because the feedback mechanism need only employ the nearest interference fringe when operating. If the piezoelectrics cannot follow the dilation the system merely jumps to the next fringe and continues the measurement. Such a system could be readily automated. Finally, the use of interference reduces the noise in the local electrical environment of the probe.

While none of the no doubt many difficulties of implementing such a scheme has been addressed it is felt that the advantages conferred would repay the effort expended.

### 7.2 Technique of self-heated expansion

In these experiments the technique of self-heated expansion has been developed and exploited along two different avenues. In the first of these the sample's resistance was used to monitor its temperature while in the second the dissipated
power allowed a calculation of the sample temperature. While both may be
operated independently, the results obtained for NbSe₃ make it clear the a
combination of these two yields the most reliable observations. The chief
advantage of this technique is that it allows a convenient absolute determination
of the sample's dilation irrespective of the cell expansion.

A dramatic improvement of this technique would be obtained by a more precise
control of the local cooling conditions of the sample. This is most easily done by
reducing the complexity of the cavity that contains the sample therefore
simplifying the calculations of heat dissipation.

The self-heated expansion technique also gives rise to the intriguing suggestion
of an AC thermal expansion technique. It appears that one of the most important
difficulties encountered in thermal expansion work is the calculation of the
coefficient of thermal expansion from the raw dilation data. The numerical
techniques brought to bear usually result in a large amount of scatter which rises
in intensity as more sensitivity is demanded from the temperature scale (as would
be the case when performing a critical exponent analysis near a phase transition).

On the other hand, a direct measurement of the thermal expansion may be
possible that would allow arbitrary sensitivity in temperature. In this case the
power consumed by the sample is driven by an AC voltage. The subsequent
expansion of the sample could then be observed by a phase-locked-loop
monitoring the modulation in the capacitance. With the prior knowledge of the
sample's thermal response to dissipated power as a function of ambient
temperature this data could be simply transformed into the coefficient of thermal
expansion without the need of a numerical derivative.

7.3 Thermal Expansion of 2H-TaSe₂

As originally conceived the basal plane dilatometric study of the layered CDW
compound 2H-TaSe₂ was intended to provide a gauge of the efficacy of the
tunnelling dilatometer. This was to be done through a comparison of the results
gathered with the two previous measurements made on this system [7.1, 7.2]. The
results eventually obtained for 2H-TaSe₂ in the vicinity of the N/ICDW phase
transition at 122 K outstripped these modest goals and lent themselves to an
extensive thermodynamic analysis.

High resolution relative dilation measurements were made in a 20 K wide range
straddling the N/ICDW phase transition. The sensitivity of the dilation
measurement was better than 0.3 ppm while the temperature resolution was, after
averaging, approximately 0.05 K. These results were only relative since no
adequate cell calibration was possible for this instrument as has been outlined
above in section 7.1. This did not prove to be a drawback for the analysis that
followed these results.

The initial observations made concluded that the N/ICDW phase transition was
exclusively second order. No evidence of a dilational discontinuity was detected near the phase transition. The second order character of the phase transition is supported by specific heat measurements [7.3] and by helium-atom surface scattering results [7.4]. Accordingly, a thermodynamic analysis was begun based on the anisotropic Ehrenfest relations appropriate to this compound. The estimated mean-field step in the thermal expansion was -2.6 ppm/K (±0.1), rather larger than the previous estimate of -0.6 ppm/K [7.2]. The associated discontinuity in the specific heat was -5.8 J/mole-K [7.3]. Together these yielded the theoretical value of -0.017 (±0.001) GPa\(^{-1}\) for the basal-plane stress dependence of the CDW phase transition temperature. The direction and magnitude of this figure were found to be comparable to the published pressure dependence of this transition, +0.020 GPa\(^{-1}\) [7.5, 7.6]. The hexagonal geometry of the crystal structure allowed a calculation of the c-axis stress dependence of this CDW transition which turned out to be -0.014 (±0.001) GPa\(^{-1}\). This figure, comparable to the basal plane dependence, argues for a significant interlayer interaction in the formation of the CDW in this layered compound. The existence of this interaction is supported by the experimental observation of CDW phase correlations in adjacent layers by neutron diffraction [7.7]. It is also required by some theories of the second-order phase transition in this compound particularly with regard to the symmetry of the basal plane CDW state [7.8].

The similarity of the thermal expansion data and specific heat results below the CDW phase transition prompted further analysis based on the mean-field
formulation of L.R. Testardi [7.9]. Testardi constructs a simplified functional form for the free energy difference between the normal and transformed phases for temperatures at and below the phase transition. This free energy difference, which is termed an "excess" quantity, is used to derive an extension of the anisotropic Ehrenfest relations for temperatures below $T_C$. Under the aegis of this analysis a more refined estimate of the basal-plane stress dependence of the CDW phase transition temperature was made using the data available below the transition. The results of a "Testardi" plot reduced the logarithmic derivative of $T_C$ with respect to basal plane stress from -0.017 GPa$^{-1}$ to -0.015 (+/-0.001) GPa$^{-1}$. The $c$-axis stress dependence suffered a similar decrease to -0.010 (+/-0.001) GPa$^{-1}$.

The application of the mean field analysis to this transition appears to be reasonable for the data available for thermal expansion and specific heat. However, these results are at odds with the changes observed in the longitudinal elastic modulus at this transition. The shift in the Young's modulus as measured by the vibrating-reed technique shows a marked rise in the modulus in the same region as the specific heat also rises [7.10]. The reverse is in fact expected on the basis of general thermodynamic considerations. It appears likely that for these CDW systems the arguments of Caille et al. may be advanced to explain this disagreement [7.11]. These authors expect that the CDW periodic lattice distortion (PLD) will principally involve those phonon modes which lie near the boundary of the undistorted Brillouin Zone (BZ). These are folded back into the
origin of the new, distorted BZ leaving the rest of the phonon spectrum unchanged. Thermodynamic properties which are calculated by an integration over the entire phonon spectrum will not be greatly affected by fluctuations in the folded-in lattice modes near the phase transition. These properties would naturally include the specific heat and the thermal expansion.

On the other hand, the appearance of a new optical mode at $q=0$ in the dispersion relation will certainly affect the slope of the acoustic branch. Thus, fluctuations in the folded-in lattice modes near the phase transition are likely to find expression in the long-wavelength acoustic properties of the sample such as those measured by the vibrating-reed technique. The more "selective" nature of the elastic measurements with regard to phonon modes may then lead to a disagreement within the Ehrenfest relations.

The foregoing discussion raises the question of fluctuations which has been so far ignored in these mean-field calculations. Observations of the specific heat anomaly at the CDW transition have been interpreted as supporting Gaussian fluctuations with a critical exponent of 1/2. [7.3]. Helium-atom surface scattering results are viewed as consistent with a 3D-XY model of the CDW transition with a critical exponent of 1/3 [7.4]. Using an integrated form of the specific heat formulation of the critical behaviour in this system the raw dilation was fitted with a range of exponents from 0.1 to 0.9. The dilation data was not well enough resolved in the region of the phase transition to allow a conclusive determination of the critical exponent. It was merely consistent with either of the models of the
phase transition.

Below the N/ICDW phase transition may be found two more transformations which work to alter the symmetry and arrangement of the CDW state in 2H-TaSe$_2$. The dilation measurements were able to show a strong anomaly near the stripe/hex phase transition at 112 K and at the Commensurate/Incommensurate (C/I) transition near 93 K. In both cases it was possible to partially suppress the anomaly by the application of stress in the basal plane. It is imagined that a systematic study of the stress dependence of these anomalies could shed some light on the thermodynamic relationship between the discommensuration (DC) lattice and these phase transitions. This is particularly interesting as it is well known that the application of uniaxial and shear stress in the basal plane can substantially alter the electrical properties [7.12, 7.13] as well as the domain arrangement in this compound [7.14].

7.4 Thermal Expansion of NbSe$_3$

The coefficient of thermal expansion of NbSe$_3$ has been obtained with fair resolution in the region of the upper CDW phase transition at 145 K. The technique used in this case was the "self-heated" expansion method which obviates the necessity for a cell calibration to extract the absolute thermal expansion. The results obtained here represent the first available for this quasi-one-dimensional compound and are rendered with an accuracy of 0.3 ppm/K and a resolution of 1
K. Attempts were made to measure the second CDW phase transition at 59 K but the fragility of the piezoelectric actuator prevented this from being successful.

The coefficient of thermal expansion extracted here shows a strong discontinuity of +1.8 (+/-2) ppm/K at 144.8 K consistent with a second order phase transition. This has been combined with the discontinuity in the specific heat which is seen to suffer a mean-field step of 64 kJ/m$^3$-K [7.15]. Under the anisotropic Ehrenfest relations the uniaxial stress dependence of the CDW phase transition temperature is simply the ratio of these two quantities, -0.028 (+/-0.003) GPa$^{-1}$. This has been found to be in close agreement with the measured value of -0.031 (+/-0.002) GPa$^{-1}$ [7.16]. In addition to the discontinuity there is also seen evidence of a small precursor "dip" in the thermal expansion which may reflect the influence of fluctuations in this system near $T_C$. Similar observations are made in the thermal expansion of the quasi-one-dimensional CDW compound "blue bronze" ($K_{0.3}$MnO$_3$) near its phase transition [7.17].

The three experimentally measured quantities, thermal expansion, specific heat and stress dependence of $T_C$, form a self-consistent set under the anisotropic Ehrenfest relations for this transition. The measured discontinuity in the longitudinal elastic modulus is four times too small to be included in this set [7.18]. Again, the reasons for this may lie in the difficulty of comparing thermodynamic quantities that depend on the "integrated" phonon spectrum with those that are more "selective" as mentioned above in section 7.3.

The positive discontinuity in the thermal expansion is found to be consistent
with a one-dimensional anharmonic model of this CDW phase transition as
proposed by M.R. Hauser et al. [7.17]. This highly idealized model of the CDW
system ignores any interchain interactions or fluctuations that might be present.
However, NbSe$_3$ may in fact be the best candidate for an experimental
comparison. One reason is that its CDW PLD is rigidly confined to the chain axis
in the upper transition [7.19]. Another is that this compound is more truly quasi-
two-dimensional than quasi-one-dimensional [7.20]. This may mean that the
influence of one-dimensional fluctuations may be damped out by interchain
correlations. Thus, it seems that this agreement may be somewhat fortuitous.

7.5 Thermal Expansion of o-TaS$_3$

The temperature dependent dilation of o-TaS$_3$ and its derived thermal
expansion have for the first time been measured with high resolution. The
technique of "self-heated" expansion allows a determination of the absolute
dilation without recourse to cell calibrations (which is perhaps the chief
advantage of this technique). Some uncertainty surrounds the question of the
correct conversion of the consumed power into temperature. It is clear that this
conversion follows either a conduction or convection-dominated model of the
surface heat dissipation for the sample. Estimates of the Nusselt number for this
system convincingly point to a conduction-dominated heat dissipation but there is
no direct evidence to support this view. Consequently, both are included in these
conclusions since it is certain that the true result will lie somewhere between these two approaches.

Whether either a conduction or convection model is employed the second order CDW phase transition in o-TaS$_3$ was always expressed as a negative discontinuity in the coefficient of thermal expansion. This observation was also independent of the degree of uniaxial strain experienced by the sample although the magnitude of the discontinuity varied considerably from sample to sample. It was not certain if this could be ascribed to the uniaxial strain or to sample-dependent effects (the latter being common to this class of CDW compounds). The magnitude of the thermal expansion discontinuity ranged from -0.4 (+/-0.1) ppm/K to -1.4 (+/-0.1) ppm/K under the conduction model and from -0.6 (+/-0.1) ppm/K to -2.0 (+/-0.1) ppm/K under the convection model. The variations showed no systematic relation to the uniaxial strain.

These results could not be compared to specific heat measurements as none are available for this particular compound. It is believed that such measurements ought to be attempted in order to resolve the apparent inconsistency that exists between the thermal expansion results and longitudinal elastic modulus observations. The Young's modulus at the CDW phase transition measured by the vibrating-reed technique suffers a 2 % decrease [7.18] while the thermal expansion and temperature dependence of the phase transition [7.16] predict a modulus increase under the Ehrenfest relations. Moreover, this modulus increase should be visible in the dilation results carried out under constant strain but no
such anomaly has been observed. It is possible that the presence of large electric fields (ca. 2 V/cm) at the phase transition in these experiments suppresses these elastic effects but little more may be said here since these experiments cannot be performed in zero electric field. It is hoped that the improvement of the "passive" mode in this instrument will make such zero field measurements possible.

A second interesting observation was made on o-TaS$_3$ when the trials were begun at temperatures below 163 K. In the case of the .18 % strain sample, and to a lesser extent in the .09 % strain sample, a marked anomaly appeared in the dilation well below $T_C$. The peak of this anomaly was found to gradually shift to higher temperatures while losing its strength as the starting temperatures climbed from 141 K to 163 K. At 163 K the anomaly disappeared altogether. No such anomalies were detected in the .51 % strain sample.

These results present a rather complicated picture of the internal CDW state in this compound. However, it seems possible that the disappearance of this anomaly above 163 K points to the existence of a phase transition at this temperature. There has been speculation concerning a C/I CDW phase transition in this temperature region. Scattering experiments have previously suggested that a continuous C/I transition takes place below 150 K in o-TaS$_3$ [7.21]. Also, recent modulus softening results have detected a sharp increase in the magnitude of elastic softening when the temperature was reduced below 160 K [7.22]. Now these dilation results may be added to the list of circumstantial evidence in favour of this phase transition. The suggestion that has been made here is that the
presence of large DC electric fields in the sample when warming or cooling through the CDW transition(s) may work to enhance the thermomechanical effect of this new transition. For example, it is noted that in blue bronze X-ray measurements detect the imposition of "frozen-in" disorder in the CDW state when the samples are cooled in high electric fields below the C/I transition [7.23]. The model proposed by these authors identifies the origin of the metastable states in blue bronze as the phase soliton lattice in the CDW state. In the commensurate state these phase solitons are widely spaced. When an electric field is imposed they will "bow" outwards in the chain direction where they encounter a random distribution of impurities. The soliton lattice coupled with the impurities form the metastable states in this compound. The interaction between the lattice and the solitons alters the thermal expansion in this system particularly when the soliton lattice is "prepared" using an electric field. It is known that strains in excess of 0.4% will suppress the metastable states in o-TaS$_3$, which suggests why this second anomaly is not detected in the .51% strain sample [7.16].

The identification of the soliton lattice as the origin of the metastable states in this system would have a profound influence on the static and dynamic properties of this system. This is particularly true with reference to the relaxation model of the threshold field softening as proposed by Brill and Roark [7.24]. While much of this remains speculation the dilation results presented here would appear to suggest that the detection of this new state below $T_c$ may be enhanced by the
application of strong electric fields.

7.6 Elastic Modulus Changes at the Threshold Electric Field in \( \sigma-\text{TaS}_3 \)

The change in the longitudinal elastic modulus at the threshold electric field has been measured for \( \sigma-\text{TaS}_3 \) in the static or zero frequency limit of mechanical vibrations. These results have shown that there is no change in the modulus to within 21 ppm for electric fields up to eight times threshold. These results have been found to be consistent with recent measurements made at mechanical frequencies below 0.1 Hz where the changes were determined to be less than 0.2 \% [7.25]. By way of contrast, measurements at 300 Hz observe a softening at the threshold field of nearly 2 \% [7.26].

The measurements made here investigate a single point in the frequency domain below 100 Hz, a domain which is held to be crucial to the theoretical description of the phenomena of modulus softening at threshold [7.24, 7.27]. The null result (to within experimental uncertainty) for this softening at zero mechanical frequency is interpreted as supporting the phase relaxation model of Mozurkewich [7.27]. However, in light of the observations made in section 7.5 on the thermal expansion of \( \sigma-\text{TaS}_3 \) it may be more appropriate to associate the relaxing object with a conjectured phase soliton lattice rather than the CDW phase itself. This may explain the seemingly low resonance for this mechanical relaxation while preserving the essential features of the relaxation model.
Appendix High Electric Field Measurements in o-TaS$_3$

This section discusses the results of electrical measurements made on o-TaS$_3$ at electric fields many times greater than the threshold field for these samples. These results do not bear directly on the elastic or mechanical properties of this material but perhaps shed some light on the coupling of the CDW to internal modes in the sample. The experiments on o-TaS$_3$ were measurements of the I-V response and its local curvature as a function of electric field and temperature. These were performed by the PLL technique described in the threshold section operated in the 2-f mode. The high resistance of this material when it enters the CDW state allows a continuous wave examination of this property without the need of a severe correction due to heating effects. The sample was a single crystal of o-TaS$_3$ mounted on a small glass slide with 4-point resistivity contacts made with Silver paint and Gold wire. The distance between the voltage contacts was 7.97 mm and this was the distance used when a calculation of the electric field was made. The cross-section of the sample was approximately 10 by 10 microns. The sample was mounted with a gentle arc in its spine so that there was little or no uniaxial strain present when cooled. The glass slide was then epoxied to the body of the probe next to the thermometer and prepared for cool-down in the usual manner. Once cooled to roughly 80 K the external heater was applied and the probe warmed at the rate of 3 K/hr. At intervals of 5 K the electric field was
gradually increased while the output of the PLL was monitored as a function of electric field. Measurements were made between 120 and 200 K. The temperature drift during each experiment was approximately 0.3 K.

A typical result of these experiments is shown in figure A.1. The principle features of this curve are first the position of the threshold field which appears as the first departure from zero slope in the curvature near 100 mV/cm. This is followed by a series of anomalies in the curvature of the I-V response as a function of applied electric field. The complete set of results are shown in figure A.2 with temperature on the third axis.

The presence of anomalies in the current-voltage response of CDW systems at large DC electric fields has been reported for the monoclinic form of TaS$_3$ [A.1] and for NbSe$_3$ [A.2]. These results may not be explained by the application of either conventional semi-classical theories [A.3] or by macroscopic tunnelling [A.4]. In either case the differential resistance is expected to decrease smoothly without any unusual topological features for DC electric fields above threshold.

There is, however, a strong similarity between the "steps" that appear in the I-V curves at high DC electric fields and the phenomena of Shapiro steps in quasi-one-dimensional CDW materials [A.5]. These Shapiro steps may be described as discontinuities in the I-V curves that result when AC electric fields in the megahertz range are applied to CDW conductors driven into their non-linear conductivity state. The effects bear a striking resemblance to similar experiments on Josephson junctions [A.6]. The physical description of this effect is one of an
Figure A.1 Typical response curve for o-TaS$_3$ here at 138 K. Maximum dissipated power in the sample was less than 0.43 microwatts. The Joule heating would be negligible.
Figure A.2  Electrical response for α-TaS$_3$ ("2f" mode second derivative of I/V curve) as a function of electric field and temperature.
interaction between an external electric field of fixed frequency and an internal electric field connected to the motion of the CDW. Associated with the onset of non-linear conductivity in the CDW compounds is a narrow-band-noise (NBN) in the current detected in the sample [A.3]. The NBN appears as a set of well-defined frequencies, a fundamental and harmonics, in the megahertz range that vary directly with the quantity of CDW-carried current. As the current in the sample is raised in the presence of an external megahertz electric field interference effects between the external frequency and the CDW frequencies associated with its motion distort the I-V characteristic. This observation is well-modelled within a semi-classical description of the CDW motion [A.7]. The remarkable characteristic of the experiments described here is that in no case were any megahertz electric fields applied to the samples.

Ortiz and coworkers [A.8] have proposed an extension of the Gruner-Zettl-Chaikin (GZC) semi-classical model [A.9] which qualitatively explains the origin of these unusual features. The usual GZC equations are modified to include a coupling to another degree of freedom within the CDW system. The degree of freedom is associated with the pinning centres but the resonant frequency required is too low to be associated with single impurities (with characteristic frequencies in the gigahertz range). This "heavier" object may be a domain wall or perhaps the lattice distorted by the CDW condensation. This extension yields two differential equations,
\[ \tau_1^{-1} \dot{x} + \omega_o^2 (x + \gamma) = \frac{eE}{m} \]  \hspace{1cm} (1)

where \( \tau_1 \) is the relaxation time of the CDW "particle", \( \omega_o \) is the frequency associated with the restoring force of the harmonic potential that the CDW particle of mass \( m \) finds itself in and \( x \) is the CDW particle position. Furthermore, the internal degree of freedom executes motion under the equation,

\[ \ddot{\gamma} + \tau_2^{-1} \dot{\gamma} + \omega_p^2 (x + \gamma) = 0 \]  \hspace{1cm} (2)

where \( \tau_2 \) is the relaxation time of the new degree of freedom, \( M \) is its mass and \( \omega_p \) is its natural frequency. The harmonic potential of the CDW is repeated for each unit cell of the CDW with cusps marking the junction of the potentials of two cells. The above equations may be solved analytically within the cell and motion examined in the passage from one cell to another. For a given electric driving field the steady-state motion yields a CDW current and a single point on the I-V curve. Ortiz et al. have explored the response of this model and find that as the CDW frequency approaches the natural frequency of the internal degree of freedom the CDW executes quasi-periodic motion transferring energy from itself to the degree of freedom. This results in a deformation of the I-V curve where the CDW current is able to satisfy this condition as shown in figure A.3 [A.8].

Under these conditions the best treatment of the data obtained in the experiments described at the beginning of this chapter would be to discard the electric field scale in favour of a CDW current scale. This is found by subtracting
the DC current fitted to a straight line below the threshold. The CDW current is then related (in α-TaS₃) to the CDW wavelength, the fraction of condensed electrons and the fundamental narrow-band-noise (NBN) frequency by,

$$J_{CDW} = n_c e \lambda f_o \quad (3)$$

The number fraction of condensed electrons varies in proportion to the size of the energy gap,

$$\frac{n_c(T)}{n_c(0)} = \frac{\pi \Delta(T)}{4k_BT_p} \quad (4)$$

and the energy gap has the BCS temperature variation,

$$\Delta(T) \propto (T_p - T)^{\frac{3}{2}} \quad (5)$$

Thus, a relative frequency scale is calculated from the CDW current from the expression,

$$f_o \propto \frac{J_{CDW}}{\sqrt{(T_p - T)}} \quad (6)$$

The absolute fraction of condensed electrons is not known. However, this conversion from CDW current to a relative frequency scale in conjunction with a NBN measurement can place an absolute scale on the frequency axis against
Figure A.3 Numerical results that show the deformation of the CDW I/V curve when the CDW executes quasi-periodic motion. (after reference A.8)
which the I-V curvature is plotted. The NBN measurement supplies the unknown scale factor. The result of such a conversion is shown in figure A.4.

Unfortunately, a NBN measurement was unsuccessful owing to the poor response of the preamplifiers used in the experiment. If the frequency scale can be properly measured then it will be possible to index the interferences shown in the curvature measurement. The systematic variation of the fundamental frequency of the internal degree of freedom with temperature would then provide an important clue concerning the origin of this mode within the CDW system.

As a final observation it is noted that a few experiments were able to measure the dilation as well as the local curvature of the I-V response (figure 6.9). In every case there was no anomaly in the dilation associated with those in the local curvature to within the noise level of 1 part in $10^7$. This null result also implies that there is no relative change in the static Young's modulus measured along the chain axis to within a figure of $2.1 \times 10^{-5}$. These results contradict the predictions of Ortiz et al. at least as far as the static elastic properties are concerned. These authors point out that their extension of the GZC model is quite similar to the those in which the CDW is elastically coupled to the lattice differing only in the treatment of the damping coefficients. On this basis they expect to see anomalies in the elastic constants associated with those in the I-V response of the system. These predictions are not borne out by experiment. It must again be emphasized, however, that the calculation of these changes in the elastic properties are usually not concerned with the static limit where our measurements are made. Thus, it is
Figure A.4 Electrical response of o-TaS$_3$ ("2f" mode second derivative of I/V curve) as a function of temperature and estimated CDW noise frequency.
not unlikely that high DC electric field experiments will show shifts in the elastic constants in vibrating-reed experiments where the system is in a mechanical mode of vibration at some finite frequency.
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