Brief Reports

Phase diagram of betaine calcium chloride dihydrate in an applied electric field

Ian Folkins and M. B. Walker
Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7

Z. Y. Chen
Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1
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The molecular crystal betaine calcium chloride dihydrate (BCCD) exhibits the largest number of structurally incommensurate and commensurate phases yet found. A model recently introduced by two of us reproduced the sequence and temperature stability interval of the commensurate phases, as well as the complex temperature dependence of the spontaneous polarization. We generalize the free energy of this model to include the effect of an applied electric field. The phase diagram of BCCD in an applied field is then calculated and the result compared with experiments.

The molecular crystal betaine calcium chloride dihydrate (BCCD) exhibits the largest number of structurally incommensurate and commensurate phases yet found. The magnitude \( \alpha(T) \) of its modulation wave vector \( k = \alpha(T) \mathbf{c}^{\ast} \) decreases from slightly below \( \frac{1}{2} \) at the initial 164-K normal-to-incommensurate transition to, successively, \( \frac{5}{16}, \frac{7}{28}, \frac{23}{36}, \frac{3}{12}, \frac{11}{12}, \frac{1}{2}, \frac{1}{11}, \frac{2}{13}, \frac{1}{2}, \frac{1}{9}, \frac{1}{8} \) and finally zero at 46.0 K. The region of temperature for which many of the commensurate phases are stable is too narrow to be measured by x-ray diffraction. In these cases, the evidence for their existence comes principally from dielectric anomalies. These measurements also indicate that there are several intervals between the commensurate phases where the wave vector appears to vary continuously.

The "devil's staircase" behavior in the wave-vector magnitude, and the associated complex temperature dependence of the spontaneous polarization and dielectric constant, have motivated several mean-field models. One of these, recently introduced by two of us, successfully explained the wave-vector sequence, reproduced the observed spontaneous polarization and was able to predict space-group symmetries for the various phases. This paper generalizes the free energy of this model to nonzero applied electric fields. Doing this enables us to calculate the temperature versus applied electric-field phase diagram, and to compare the result with what is known about this diagram from experiment.

The normal-state crystal structure of BCCD contains four BCCD molecules within its orthorhombic unit cell. We envisage this structure as being composed of layers perpendicular to the \( c \) axis. The layers are not identical, however, as the \( c \)-axis periodicity is twice the interlayer spacing. The soft mode responsible for driving the normal-to-incommensurate transition, and presumably the subsequent transitions at lower temperatures as well, is known to be of \( \Lambda_3 \) symmetry. The approach of Ref. 4 examines the displacements of the atoms in a particular layer caused by this mode. The wave vector of the \( \Lambda_3 \) mode is perpendicular to the layers. Hence, the relative displacements of any two ions in the same layer is prescribed by the polarization vector of the \( \Lambda_3 \) mode. In general, these displacements will not transform according to any single irreducible representation (IRREP) of the two-dimensional space group of a layer. They can, however, be split into two parts, one part transforming according to the \( \Gamma_1 \) two-dimensional IRREP and the other to the \( \Gamma_2 \) IRREP. The amplitude on layer \( l \) of the first part is referred to as \( v_l \), the amplitude of the second as \( w_l \). Symmetry preserves to some extent what the ion displacements in the \( v_l \) and \( w_l \) symmetry modes are. For example, the two symmetry-related calcium ions of the two-dimensional unit-cell move in opposite directions along the \( b \) axis for \( v_l \), but in the same direction for \( w_l \).

The ratio between \( v_l \) and \( w_l \) is independent of \( l \) for a particular \( \Lambda_3 \) mode. One can, however, relax this constraint to consider more general displacements from the normal state. The Landau model of Ref. 4 considers all \( v_l \) and \( w_l \) to be independent variables. The free energy of an isolated layer \( l \) is expanded to fourth order in powers of \( v_l \) and \( w_l \). The two-dimensional symmetry of a layer will determine the form of this expansion. Interlayer interactions are represented by products of \( v_l \) and \( w_l \) with \( v_{l+1} \) and \( w_{l+1} \). The form of these nearest-neighbor layer coupling terms will depend on the full three-dimensional

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space group of BCCD. The resulting free energy can be shown to be,

\[ F_0 = \sum \left( \frac{1}{2} \alpha_v^2 + \frac{1}{2} \beta_v^2 + \frac{1}{2} \alpha_p^2 + \frac{1}{2} \beta_p^2 + \frac{1}{2} \beta_{vp}^2 \right) + \frac{1}{2} \sum (J_{i,j} + J') \omega_i \omega_{i+1} \]

\[ + \frac{1}{2} \sum (\omega_i \omega_{i+1} - \omega_{i+1} \omega_i) . \]

(1)

It should be valid as long as the displacements of a layer are small and the interactions between layers short ranged. The interlayer interaction terms will prescribe the variation in \( v_i \) and \( w_i \) as one goes from layer to layer. It is the competition between these terms that gives rise to the sensitive dependence of the modulation wave vector on changes in the parameters \( J \) and \( J' \). Instead of using the parameters of Eq. (1), however, the authors of Ref. 4 introduce the parameters \( a = \frac{1}{2}(\alpha + \alpha') \), \( J = \frac{1}{2}(J + J') \), and \( b \). They fix \( a = 0.4 \), \( J = 0 \), \( b = 3 \) and calculate the \( a \) versus \( J + \) phase diagram. Their result is shown as Fig. 1. The trajectory \( a = 0.8J + 1.6 \) reproduces not only the succession of commensurate phases observed, but also their approximate temperature intervals, assuming \( J + \) varies linearly with temperature.

The free energy of Eq. (1) is expanded in terms of the displacements alone. An electric field applied to the crystal, however, will not interact with the displacements directly but rather through the crystal's polarization. Hence, to consider the effect of an electric field on BCCD, it is necessary to first couple the displacements with the polarization, and then the polarization with the field. The electric fields applied to BCCD and the average polarizations per layer of BCCD along the \( a \) and \( b \) directions will be referred to as \( E_a, P_a \), and \( E_b, P_b \), respectively. They will transform as vector components while the transformation properties of \( v_i \) and \( w_i \) are given in Ref. 4. These symmetries will dictate the lowest-order couplings between the displacements and polarization, and polarization and field. They are,

\[ F_e = \frac{m}{2} \chi_{0b}^{-1} P_a^2 + \frac{m}{2} \chi_{0b}^{-1} P_b^2 - mP_a E_a - mP_b E_b \]

\[ + c_{a1} P_a \sum \left( -1 \right) v_i (w_{i+1} - w_{i-1}) \]

\[ + c_{a2} P_a \sum \left( -1 \right) v_i^2 + c_{a3} P_a \sum \left( -1 \right) w_i^2 \]

\[ + c_b P_b \sum w_i , \]

(2)

where \( m \) is the number of layers. Note that the displacements interact linearly with \( P_b \) but quadratically with \( P_a \). This accounts for the relative weakness of the spontaneous \( P_a \) as compared to spontaneous \( P_b \) seen in experiments.

At equilibrium, the free energy \( F_e \) must be a minimum with respect to \( P_a \) and \( P_b \). This condition can be used to solve for the polarizations in terms of the displacements and applied fields. The resulting expression for \( P_a \) involves four terms—a term linear in \( E_a \), and the \( c_{a1}, c_{a2}, \) and \( c_{a3} \) terms quadratic in the displacements. The last three terms were discussed in Ref. 4, where it was found that each made a similar contribution to the spontaneous \( a \) polarization. They therefore considered only the \( c_{a1} \) term and set \( c_{a2} = c_{a3} = 0 \). We will assume that this can be done for nonzero applied fields as well. The resulting simplified expression for \( P_a \), and the corresponding expression for \( P_b \) can be substituted into Eq. (2) to obtain the free energy \( F_e \) in terms of the displacements and fields alone. The result is

\[ F_e = E'_a \sum ( -1) v_i (w_{i+1} - w_{i-1}) \]

\[ - \frac{1}{2} c_{a1} E_a \sum v_i (w_{i+1} - w_{i-1})^2 \]

\[ + E'_b \sum w_i \left( -\frac{1}{2} c_{a2} \right) \sum (w_i)^2 . \]

(3)

Terms involving the fields alone are dropped since they can be assumed fixed at some applied value. The parameters have been scaled for simplification. For example, \( E'_a \) has been substituted for \( c_{a1} \chi_{0b} E_a \) and \( c'_{a1} \) for \( c_{a1} / \sqrt{\lambda_{0a}} \). Similar remarks apply to \( E'_b \) and \( c'_{b} \).

The equilibrium displacements \( v_i \) and \( w_i \) in an applied field will be those which minimize the total free energy \( F_0 + F_e \). They will now therefore depend on seven parameters—the five originally occurring in \( F_0 \) and the \( c_{a1}' \) and \( c'_{b} \) of Eq. (3). Note that the \( c_{a1}' \) and \( c'_{b} \) terms may contribute to the total free energy even if there are no applied fields. These terms were not considered in Ref. 4 because they couple the displacements of layers arbitrarily far apart. Their introduction here means that the stable states in zero field associated with the free energies \( F_0 \) and \( F_0 + F_e \) will, in general, be different. However, since \( F_0 \) alone was able to successfully reproduce the wave-vector sequence of BCCD, we will set \( c_{a1}' = c_{b}' = 0.001 \). This renders the effect of these additional terms small and enables us to set \( a = 0.4, J = 0, \)

FIG. 1. This is the zero field \((J_+, a_+)\) phase diagram calculated in Ref. 4 with \( a = 0.4 \), \( J = 0 \), and \( b = 3 \). The low-order commensurate phases have been labeled by their value of \( a \). The shaded regions correspond to higher-order commensurate phases and/or incommensurate phases. The trajectory shown approximately reproduces the succession of wave vectors seen in experiment and their temperature-stability intervals.
\( b = 3 \), and \( a_+ = 0.8 J_+ + 1.6 \) as in Ref. 4. We will show that this choice of parameter values is consistent with the stable states and polarizations seen in BCCD when an electric field is applied along its \( b \) direction. It is not our intent to suggest, however, that this choice is uniquely able to explain the response of BCCD to an electric field. There may be other sets of values which do equally well or better.

The free energy \( F_0 + F_e \) can be used to calculate the phase diagram of BCCD in either an applied \( E'_b \) or \( E''_b \). Only the \( E'_b \) diagram is given here because few experiments have measured the effect of an \( E'_b \) field on BCCD. The phase at a given point \( (J_+, E'_b) \) in the diagram is characterized by the periodicity of its displacements. These can be determined by extending the numerical methods used to minimize \( F_0 \) in Ref. 10. This procedure determines the best displacements with periodicity \( \alpha = n / m \). In our case, this is done for all ratios \( n / m \) with \( m \leq 26 \). The displacements which yields the overall minimum determine the stable state.

Figure 2 shows that the stability of states \( n / m \) with \( n \) even and \( m \) odd is favored by the application of a field while for the others it is progressively diminished. These states are known to exhibit a spontaneous \( b \) polarization. In this case, Eq. (2) implies that they have \( P_b \propto \sum u \neq 0 \) for \( E'_b = 0 \). The third term on the right-hand side of Eq. (3) then gives a contribution to the free energy linear in \( E'_b \). The field will always favor the domain that makes this contribution negative. For the other states, the leading term is, at most, quadratic in \( E'_b \). The lowest-order effect of \( E'_b \) is therefore to always favor the spontaneously polar states.

Figure 2 can be compared with the phase diagram of Kopperpieper et al. 

They have determined the regions of stability of the \( \frac{1}{3}, \frac{1}{2}, \frac{1}{4}, \frac{1}{5}, \frac{1}{6}, \) and \( \frac{2}{3} \) states. Their phase boundaries are in rough agreement with those seen in Fig. 2. Our phase diagram, however, shows additional higher-order phases. Their existence is verified by hysteresis loop measurements that plot \( P_b \) against \( E_b \) for some fixed temperature. This corresponds, in our diagram, to the polarizations one would encounter by starting off at a particular \( J_+ \) and going in the \( E'_b \) direction. The steplike behavior seen in the loops can be compared with the discontinuities in the polarization to be expected when crossing first-order lines in our phase diagram. These discontinuities can be evaluated using the expression for \( P_b \) in terms of \( E'_b \) and \( \omega \), that, as previously discussed, can be obtained from Eq. (2). The results are shown in Figs. 3 and 4. The five plots of Fig. 3 can be compared with the ten loops measured by Inruh et al. 

The \( J_+ = -0.767 \) plot corresponds to their first loop at 116.8 K. Both have an \( E'_b = 0 \) phase which is nonpolar and a discontinuity in \( P_b \) associated with a field-induced transition to the \( \frac{2}{13} \) state. Unruh et al. 

then give several loops showing the movement of the discontinuity to smaller field values as the stability interval of the \( \frac{2}{13} \) state is approached. This behavior would be reproduced by our diagram. The plot at \( J_+ = -0.775 \) shows the spontaneous polarization of the \( \frac{2}{13} \) state. One encounters a nonpolar state below \( \frac{1}{13} \) and the \( \frac{2}{13} \) discontinuity again moves off to larger fields. This is shown for \( J_+ = -0.782 \). The remaining two loops of Unruh et al. 

are taken from the polar \( \frac{2}{13} \) and nonpolar \( \frac{1}{13} \) states. The response of their polarizations to an applied field is well reproduced by our \( J_+ = -0.786 \) and \( -0.788 \) plots, respectively.

Rother et al. 

have measured another set of hysteresis loops at 12 different temperatures. Their loops at 124.1, 116.6, 77.1, 75.0, 59.0, and 50.5 K may be compared with ours at \( J_+ = -0.72, -0.761, -0.924, -0.95, -0.99, \) and \(-1.032, \) respectively. The overall agreement is quite good. We have, however, discontinuities arising from transitions to the \( \frac{5}{13}, \frac{4}{13}, \) and \( \frac{3}{13} \) phases in our \( J_+ = -0.761 \) plot not seen in their loop at 116.6 K. It is possible that a more sensitive measurement would have seen these additional discontinuities. It is also possible that Fig. 2 overestimates the stability of these states. If this region of the phase diagram was incommensurate, the wave vector would vary continuously with \( E_b \) and

![FIG. 2. Our calculated phase diagram of BCCD in an applied \( E'_b \) field. The phases have been labeled by their value of \( \alpha = n / m \) and only those with \( m \leq 26 \) have been considered. The \( E'_b = 0 \) axis corresponds to the trajectory shown in Fig. 1.](image-url)
there would be no discontinuities in the polarization. Modifying our numerical procedure to deal with incommensurate states may resolve this discrepancy. The 77.1-K loop of Rother et al.\textsuperscript{12} has a zero-field discontinuity in the polarization. This is explained by our $J_+ = -0.924$ loop as due to the existence of the spontaneously polar $\frac{4}{15}$ state, though it is apparently not known to be stable at zero field. The lower-temperature hysteresis loop measurements seen to indicate that the $\frac{4}{15}$ state occupies a region of stability between the $\frac{2}{11}$ and $\frac{5}{18}$ phases. Its absence in our diagram is probably because, as explained in Ref. 4, our trajectory underestimates $a_+$ in this temperature region. In conclusion, we note that our previously introduced competing interaction model is consistent with the stable states and polarizations which arise when an electric field is applied along the $b$ direction of BCCD.

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