Thermodynamic characterization of the low-temperature phase transformations in KOH and KOD

Mary Anne White, Allyson Perrott, Debra Britten, and Michiel J. M. Van Oort

---

Articles you may be interested in

On low-temperature polyamorphous transformations
Low Temp. Phys. **32**, 868 (2006); 10.1063/1.2356844

Friction-induced nonequilibrium phase transformation of low-temperature ice
J. Appl. Phys. **97**, 043525 (2005); 10.1063/1.1852722

Effect of an orientational phase transformation on low-temperature creep in n- H 2
Low Temp. Phys. **27**, 949 (2001); 10.1063/1.1421461

Mechanisms of phase transformation in low-temperature irradiated NiAl
J. Appl. Phys. **65**, 1499 (1989); 10.1063/1.342964

Effect of Stress on the Low-Temperature Phase Transformation in V3Si
J. Appl. Phys. **37**, 3447 (1966); 10.1063/1.1708879

Thermodynamic characterization of the low-temperature phase transformations in KOH and KOD

Mary Anne White,[a] Allyson Perrott, Debra Britten, and Michiel J. M. Van Oort[b]

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

The heat capacities of KOH and its deuterated analog KOD have been measured over the temperature range $17 < T < 342$ K and $32 < T < 295$ K, respectively. The thermodynamics of the phase transformations to the low-temperature antiferroelectric phases have been characterized: T_{tr} (KOH) $= 226.7 \pm 0.2$ K; T_{tr} (KOD) $= 253.1 \pm 0.1$ K; ΔS_{tr} (KOH) $= 0.121 \pm 0.002$ R; ΔS_{tr} (KOD) $= 0.1258 \pm 0.0007$ R. The thermodynamic changes are consistent with tunneling of the hydroxide (deuteroxide) ions between two minima in a double-well potential.

I. INTRODUCTION

Recent studies of alkali metal hydroxides and deuteroxides at subambient temperatures have shown, in some cases, a new low-temperature phase. For example, in NaOD there is a phase transformation at $T = 153.2$ K from the room-temperature orthorhombic structure (*Bmmb*, $Z = 4$) to a low-temperature monoclinic phase ($P2_1/a, Z = 4$).[1-6] This first-order transformation, which is driven by the softening of a transverse optic mode, does not appear to have an analog in NaOH at atmospheric pressure.[4]

Recent studies of KOH and its deuterated form KOD have shown that both undergo low-temperature phase transitions.[7,8] As in the case of NaOD, the hydroxide (deuteroxide) ions are, on average, aligned along the orthorhombic c axis at room temperature, and canted away from that axis at lower temperatures such that the low-temperature form is antiferroelectric.

The chemical simplicity of the alkali metal hydroxides makes this system of considerable theoretical interest. In addition, experimental studies of the hydroxides and deuteroxides may help us understand more complex ferroelectric/antiferroelectric systems. Furthermore, it would be useful to have further knowledge of the behavior of the hydroxide and deuteroxide ions in the solid state, in light of the recent finding that alkali metal hydroxides can induce a low-temperature ordered phase of ice.[9]

Although low-temperature phase transitions have been detected in KOH and KOD, accurate thermodynamic parameters for these phase transitions have not been available. In order to understand fully the nature of these transitions, it is essential to have this fundamental information.

II. EXPERIMENTAL

KOH was prepared by drying KOH (Alpha ultrapure) in vacuum at 160 °C in a zirconium crucible in an Abderhalden drying apparatus.[10] The KOD samples were prepared in a similar manner by dehydration of KOD in D_2O (gold label, $> 99\%$ D, Aldrich).

Alkali metal hydroxides are extremely hygroscopic, and therefore the water contents of the measured samples were determined. In our earlier studies with NaOD, we were able to make this characterization through the measurement of the NaOD·D_2O eutectic at 337 K.[1,6,11] Using differential scanning calorimetry, we detected endotherms with onset temperatures of 377 K in KOH and at 360 K in KOD, which diminish with further drying, and from the KOH/H_2O phase diagram[11] we find that these correspond to the monohydrate eutectic. The enthalpy change for the melting of KOH(D)·H(D)$_2$O does not appear to have been measured previously. We assumed that it is the sum of the enthalpy of fusion of NaOH·H_2O (which takes place at 62 °C[1,11]) and the molar enthalpy of vaporization of water, since the eutectic for the potassium salts is not complete until above the boiling point of water. Based on this assumption, our KOH sample contained 0.05 mass % H_2O, and our KOD sample contained 0.16 mass % D_2O.

The other major impurity problem in alkali metal hydroxides is carbonate. The only way to keep the level of this impurity low is to minimize the exposure of the sample to air. From powder x-ray analysis[12] we found the carbonate level to be 2.8 mass % in the KOH sample, and undetectable (< 1 mass %) in the KOD sample.

The ^2H content of the KOD samples was determined by the measurement of the ^1H H_2O signal in a D_2O solution of KOD relative to a series of KOH/D_2O standard solutions; the $^2H/^1H$ ratio of the KOD sample was 40.7:1 (i.e., 97.6 mol % ^2H).

The heat capacities of 20.6911 g of the KOH sample and 6.0031 g of the KOD sample were measured by adiabatic calorimetry. The KOH measurements were carried out from $T = 17$ to 342 K, in a large-scale calorimeter.[13,14] The KOD measurements were made in a new smaller-scale calorimeter[15] between $T = 32$ and 295 K. All the measurements were made using the heat-pulse technique, as described in detail elsewhere.[13-15] The precision and accuracy of both calorimeters, as determined by the measurement of Calorimetry Conference Standard benzoic acid, were within $\pm 1\%$.

III. RESULTS AND DISCUSSION

The heat capacity results for KOH and KOD are given in Tables I and II, respectively. There was no dependence in

---

TABLE I. The experimental heat capacities of KOH.

T (K)	C_p (R)	T (K)	C_p (R)	T (K)	C_p (R)
16.65	0.214	193.61	6.529	246.68	7.984
20.39	0.256	197.53	6.659	249.20	7.968
22.90	0.325	201.64	6.774	254.24	7.995
25.02	0.402	203.98	6.893	254.42	8.002
26.74	0.430	204.09	6.906	258.41	7.997
28.56	0.446	206.36	7.007	259.02	8.024
30.43	0.562	208.77	7.129	261.83	8.022
32.90	0.704	210.64	7.260	268.70	8.114
35.56	0.856	211.21	7.271	269.49	8.091
39.14	1.083	212.36	7.366	271.91	8.105
43.55	1.356	213.63	7.440	272.50	8.089
48.31	1.688	213.67	7.463	277.22	8.196
53.23	2.010	216.16	7.637	283.14	8.203
58.38	2.329	217.09	7.658	285.00	8.190
63.58	2.556	217.80	7.798	285.04	8.175
68.14	2.839	218.50	7.867	286.70	8.186
72.27	3.046	218.57	7.874	292.91	8.238
76.56	3.283	218.67	7.809	297.65	8.291
81.09	3.509	219.22	7.929	298.27	8.300
85.84	3.702	220.02	7.971	300.84	8.310
90.72	3.888	221.15	8.150	300.99	8.301
95.67	4.074	221.61	8.291	308.78	8.406
100.68	4.250	222.83	8.286	311.68	8.407
105.72	4.396	223.43	8.531	312.29	8.452
110.78	4.552	223.66	8.600	315.41	8.409
115.57	4.692	225.24	8.781	316.75	8.432
120.07	4.784	225.30	8.865	324.40	8.605
124.58	4.902	226.05	9.174	325.25	8.596
127.64	5.020	226.07	9.261	327.04	8.621
129.10	5.046	226.83	9.359	332.17	8.653
133.64	5.142	227.21	9.204	338.96	8.739
139.07	5.237	227.61	9.042	339.97	8.730
139.11	5.272	228.02	8.917	341.71	8.775
141.87	5.356	228.06	8.903		
145.53	5.413	228.68	8.574		
149.03	5.505	229.25	8.310		
151.97	5.529	229.42	8.240		
152.58	5.521	229.47	8.162		
158.42	5.668	229.67	8.021		
164.90	5.805	230.09	7.990		
166.18	5.835	230.51	7.925		
171.38	5.951	230.93	7.921		
177.89	6.151	231.11	7.942		
179.87	6.155	231.68	7.909		
184.43	6.280	233.97	7.885		
185.11	6.354	236.27	7.886		
190.98	6.455	238.57	7.900		
192.37	6.523	244.41	7.919		

TABLE II. The experimental heat capacities of KOD.

T (K)	C_p (R)	T (K)	C_p (R)	T (K)	C_p (R)
32.47	0.705	161.10	5.866	249.43	9.435
36.02	0.888	164.99	5.958	249.66	9.626
40.12	1.221	168.83	6.040	249.90	9.763
44.53	1.469	172.82	6.130	250.12	9.738
49.53	1.791	176.58	6.208	250.37	9.745
54.53	2.058	180.67	6.300	250.61	9.873
59.55	2.353	184.34	6.379	250.85	10.05
64.53	2.625	188.52	6.489	251.08	10.01
69.38	2.870	192.09	6.567	251.32	10.05
74.12	3.116	196.40	6.663	251.55	10.12
78.81	3.342	199.85	6.731	251.77	10.10
81.07	3.409	204.84	6.839	251.99	10.26
83.47	3.524	207.62	6.924	252.21	10.33
84.94	3.616	212.15	7.057	252.43	10.35
88.00	3.733	215.39	7.153	252.65	10.45
88.41	3.764	220.04	7.305	252.85	10.73
89.63	3.803	223.16	7.415	253.07	10.78
92.61	3.923	227.93	7.598	253.29	10.55
94.33	3.987	230.77	7.718	253.71	10.51
95.94	4.053	235.20	7.987	253.95	10.24
97.20	4.094	235.69	8.039	254.18	9.819
99.03	4.151	235.86	8.020	254.25	9.753
101.81	4.246	238.48	8.225	254.40	9.646
103.46	4.307	240.06	8.337	254.64	9.491
106.42	4.394	241.54	8.388	255.11	9.248
111.02	4.559	242.01	8.427	255.47	9.088
111.03	4.546	242.46	8.517	255.94	8.912
115.07	4.687	242.93	8.584	258.21	8.980
115.64	4.694	243.38	8.631	262.27	8.960
118.62	4.785	243.83	8.706	262.68	8.977
120.27	4.820	244.30	8.724	264.59	9.007
122.84	4.906	244.76	8.838	264.81	8.985
124.89	4.960	245.63	8.886	270.32	9.006
126.27	5.014	246.33	8.875	270.62	9.005
130.50	5.128	246.66	8.938	272.36	9.035
133.95	5.219	246.99	9.066	272.70	9.018
138.09	5.337	247.33	9.086	278.43	9.001
141.67	5.430	247.65	9.249	278.60	9.033
145.68	5.532	247.98	9.272	280.58	9.010
149.41	5.615	248.31	9.471	286.51	9.070
153.37	5.699	248.64	9.505	286.59	9.076
157.18	5.791	248.95	9.421	288.55	9.074
				294.57	9.031
				294.58	9.018

capacity at the transition temperature. The base line heat capacities, for the purposes of evaluating ΔH_{tr} and ΔS_{tr}, have been taken in each case to be the experimental heat capacity from a temperature 30 K below the transition tem-

either case on the thermal history of the sample, and the results, therefore, are given in order of increasing temperature.

Figure 1, the heat capacities of KOH and KOD as functions of temperature, clearly shows the phase transitions in these salts. At first glance, the two phase transitions appear rather similar, and detailed thermodynamic considerations bear this out.

The transition temperature is taken as the temperature of the maximum in C_p from a run using very small ($\sim$0.2 K in this case) temperature increments. In order to determine the enthalpy and entropy changes at a transition, it always is necessary but somewhat arbitrary to determine the "base line" heat capacity, i.e., the heat capacity as it would have been had the transition not taken place. In the case of KOH and KOD, both C_p curves show a definite "step" in the heat
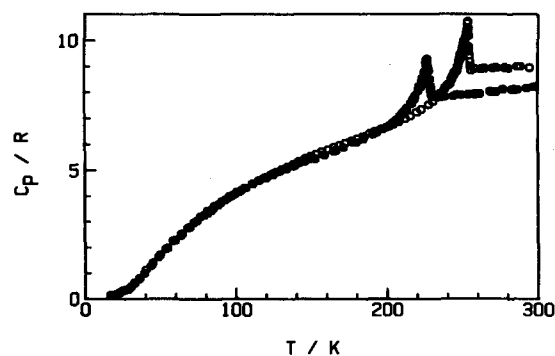

FIG. 1. The experimental molar heat capacities of KOH (closed circles) and KOD (open circles) as a function of temperature.

perature extrapolated forward to the transition temperature, and the experimental heat capacity from 15 K above the transition temperature extrapolated back to the transition temperature. The C_p step at the transition is 0.72 R for KOH and 1.07 R for KOD. The transition enthalpy was calculated from the enthalpy required to take the sample from below the transition region to above it, less the base line enthalpy change. The transition entropy was calculated similarly from the integration of C_p/T. The thermodynamic descriptors of the low-temperature phase transitions in KOH and KOD are summarized in Table III.

There are a few sources of information with which we can compare our phase transformation data for KOH and KOD. For KOH this is limited to the dielectric and differential scanning calorimetric (DSC) investigations of Bastow *et al.*,[7] in which the transition temperature is reported as 233 K; as expected for their scanning technique, this is in fair agreement with our more accurate (equilibrium) determination of 226.7 K. No determination of the transition enthalpy appears in the literature.

Similarly, the dielectric and differential scanning calorimetric experiments with KOD[7] give a transition temperature of 257 K and a further differential scanning calorimetric experiment[8] shows the transition to be at 251 K; these compare favorably with our value of 253.1 K. From the DSC experiment of Mach *et al.*,[8] the transition enthalpy was found to be 50 J mol^{-1}. This value is considerably less than what we find (257 J mol^{-1}), and the difference likely is due to the presence of moisture in their sample. It is known that a small amount of moisture can reduce the magnitude of the low-temperature transition in KOD[16] and the thermal anomaly reported by Mach *et al.*[8] at 366 K and attributed to a KOD phase transformation is in fact due to the melting of KOD$\cdot$D$_2$O.[11] Furthermore, we found in our measurements that with one KOD sample that contained 0.9 mass % water due to a problem in the sample loading procedure there was no evidence for a low-temperature phase transition.

A summary of the comparison between KOH and KOD is as follows. Below $\sim T = 70$ K, the heat capacity of KOH is slightly less than that of KOD. From $\sim T = 70$ to 90 K, the heat capacity of KOH is slightly greater. From $\sim T = 90$ to 120 K, the heat capacities of KOH and KOD are very similar. From $\sim T = 120$ K until the transition region, the heat capacity of KOH is less than that of KOD, and this also is the case above the transition. These results are as for NaOH/D,[6] viz., the heat capacity generally is greater for the deuterated compound. The transition temperature of KOH is considerably lower than that of KOD, reflecting the lower barrier to thermal excitation of the appropriate mode in the hydrogenous material, consistent with tunneling of the H(D)'s across the double-well potential.[7] The entropy changes associated with the low-temperature transitions in KOH and KOD are essentially the same. (Slight differences shown in Table III likely are assignable to the choice of the base line heat capacity.)

As in NaOD,[6] the transition entropies in KOH and KOD are insufficient to account for independent ordering of

TABLE III. The thermodynamics of low-temperature transitions for some alkali metal hydroxides.

	T_{tr} (K)	ΔH_{tr} (J mol^{-1})	ΔS_{tr} (R)	Reference
KOH	226.7 $\pm$ 0.2	222 $\pm$ 3	0.121 $\pm$ 0.002	this work
KOD	253.1 $\pm$ 0.2	257 $\pm$ 2	0.1258 $\pm$ 0.0007	this work
NaOD	153.2 $\pm$ 0.1	131.1 $\pm$ 0.7	0.1039 $\pm$ 0.0006	Ref. 6

the dipoles, as this would amount to $R \ln 2$ (= 0.693 R), considerably greater than observed (0.121 R for KOH and 0.1258 R for KOD). The phase transformations in the alkali metal hydroxides appear to be similar to the low-entropy phase transformations in antiferroelectrics such as NH$_4$H$_2$PO$_4$ and its analogs, where tunneling of the protons (or deuterons) also plays an important role. The large shift of the phase transition on deuteration in KOH/D also is consistent with tunneling; the energy levels of the deuterated compound are lower in the wells and hence the heavier isotopomer effectively has a wider barrier through which to tunnel. Further evidence for the importance of tunneling is the large effect of changing the alkali metal, as the transition entropies of KOH and KOD are similar to each other, but about 20% greater than in NaOD.

ACKNOWLEDGMENTS

[1]D. T. Amm, Ph.D. thesis, Queen's University, Kingston, Canada, 1985.
[2]D. T. Amm, T. J. Bastow, K. Jeffrey, R. D. Heyding, and S. L. Segel, Thermochim. Acta 95, 447 (1985).
[3]T. J. Bastow, D. T. Amm, S. L. Segel, and R. D. Heyding, Z. Naturforsch. Teil A 41, 283 (1986).
[4]S. Elschner and T. J. Bastow, Solid State Commun. 60, 75 (1986).
[5]T. J. Bastow, M. M. Elcombe, and C. J. Howard, Solid State Commun. 57, 339 (1986).
[6]M. A. White and S. A. Moore, J. Chem. Phys. 85, 4629 (1986).
[7]T. J. Bastow, M. M. Elcombe, and C. J. Howard, Solid State Commun. 59, 257 (1986).
[8]B. Mach, H. Jacobs, and W. Schafer, Z. Anorg. Allg. Chem. 553, 187 (1987).
[9]T. Matsuo, Y. Tajima, and H. Suga, J. Phys. Chem. Solids 47, 165 (1986).
[10]Arthur I. Vogel, *Textbook of Practical Organic Chemistry*, 4th ed. (Longman, London, 1978), p. 121.
[11]A.-P. Rollet and R. Cohen-Adad, Rev. Chim. Miner. 1, 451 (1964).
[12]*Powder Diffraction File Search Manual, Hanawalt Method, Inorganic*, edited by L. G. Berry (Joint Committee on Powder Diffraction Standards, Swarthmore, PA, 1976).
[13]M. A. White, Thermochim. Acta 74, 55 (1984).
[14]M. J. M. Van Oort and M. A. White, J. Chem. Soc. Faraday Trans. 1 81, 3059 (1985).
[15]M. J. M. Van Oort and M. A. White, Rev. Sci. Instrum. 58, 1239 (1987).
[16]T. J. Bastow (private communication, 1986).