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Thermodynamic properties of RbH_2AsO_4

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Calorimetric and dielectric measurements have been made on RbH_2AsO_4 in the vicinity of the temperature of the ferroelectric transition 109.75 K. The transition is found to be first order with latent heat 255 ± 5 J/mole. The total transition entropy is found to be $0.50R$. The Curie constant is found to be 223 K. These results differ considerably from the predictions of the conventional static hydrogen-bond-occupation model, a fact which can be interpreted as demonstrating that dynamic effects are more important in RbH_2AsO_4 than in KH_2AsO_4 .

As part of an investigation of order-disorder ferroelectrics isomorphous to potassium dihydrogen phosphate (KDP), we recently reported¹ on calorimetric and dielectric measurements of potassium dihydrogen arsenate (KDA) and its deuterated isomorph (DKDA). More recently, this type of information has become available for cesium dihydrogen arsenate (CDA) and its deuterated isomorph (DCDA).^{2,3} This paper reports the results of similar measurements conducted on rubidium dihydrogen arsenate (RDA), a member of the KDP family which undergoes a first-order transition at $T_C = 109.75$ K. The first-order nature of the transition in RDA was first established by Blinc, Burgar, and Levstik⁴ on the basis of hysteresis in the dielectric measurements. In the calorimetric measurements, a latent heat is observed. As in the previous paper, the experimental results are compared with the hydrogen-bond-occupation model of Silsbee, Uehling, and Schmidt⁵ (SUS).

I. EXPERIMENTAL MATTERS

The apparatus and procedures used for these measurements have been described previously.¹ The measurements were conducted using a sample consisting of two single crystals obtained from Quantum Technology.⁶ Each crystal has nominal dimensions $1 \times 1 \times \frac{1}{2}$ cm and a mass of approximately 1.8 g. For dielectric measurements, a gold electrode, approximately 1000 Å thick, was deposited by evaporation on one z face of each crystal. A gold foil sandwiched between the uncoated z faces of the two crystals served as the other electrode, which was electrically grounded. The capacitance of the sample was measured at 1 kHz to determine the dielectric constant. The necessary addendum for calorimetric measurements (sample heater, control thermocouple, and temperature-measuring thermistor) was attached to the gold foil.

The heat capacity of the addendum was established on the basis of previous measurements in this laboratory of addenda of similar composition.

The addendum contribution to the total heat capacity was at most 7.5% and was considerably smaller than this in the region of the ferroelectric transition. The transition was found to be first order, occurring at $T_C = 109.75$ K, with a latent heat of 225 ± 5 J/mole. The specific-heat data are shown in Fig. 1.

An interesting feature of the specific heat is an anomalous spike that occurs at 109.0 K and which is shown on an expanded scale in the inset of Fig. 1. This feature was quite repeatable and was accompanied by small anomalies in the susceptibility and dielectric dissipation as functions of temperature. The extreme narrowness of this feature means that it contains but little entropy, approximately 0.5% of the total transition entropy. Similar, although less pronounced, anomalies have been observed in most of the other KDP-type materials investigated to date, but the significance, if any, of this feature has no ready explanation.

In calorimetric measurements of ferroelectric transitions, the quantity of interest is that part of the specific heat due to changes in the ferroelectric polarization (ΔC), which is the difference between the measured specific heat (C_E) and the specific heat that would be measured at constant polarization (C_P). It is considered that C_P represents the lattice specific heat. We have used a linear approximation to C_P , which is given by the straight lines in Fig. 1. This line was determined by assuming that $C_E = C_P$ above T_C . If one assumes that C_P has the same temperature dependence above and below the transition—an assumption which seems reasonable based on the abruptness of the transition and the temperature dependence of the heat capacity of isomorphous crystals in this temperature range—it is necessary to assume that a discontinuity of about $0.4R$ occurs in C_P at T_C . Similar behavior was observed in KDP,⁷ DKDA,⁸ CDA,³ DCDA,⁴ and DKDA, although a discontinuity in C_P was not observed in KDA. The strongest evidence that this is a real effect and not the result of an incorrect assignment of C_P comes from

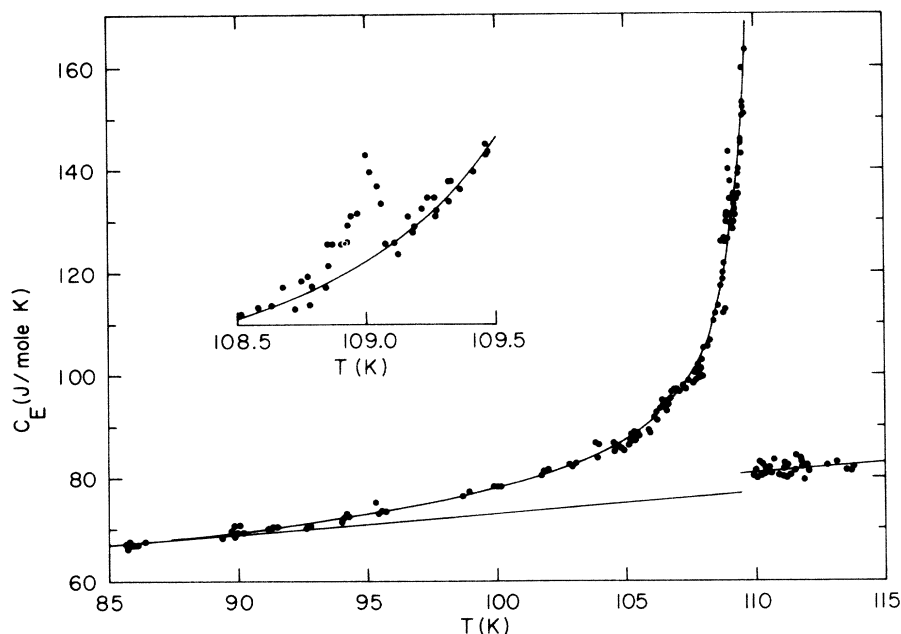


FIG. 1. Heat capacity of RbH_2AsO_4 in the vicinity of the ferroelectric transition. The lower solid line shows the values assumed for C_P . The inset in the upper-left portion of the figure shows the anomalous behavior observed near 109.0 K in more detail, with the curve representing the trend of the data outside the anomalous region.

the electrocaloric measurements conducted on KDP, which allow C_P to be determined directly and which show a similar discontinuity in C_P .⁷

Considerable effort was expended attempting to make electrocaloric measurements on RDA so as to verify the assignment of C_P and to verify the indirect polarization determinations discussed below. As in the case of KDA,^{1,9} such measurements proved infeasible because of inability to obtain a fully polarized sample, inability to cause polarization reversal in any but a highly irreversible fashion, and anomalous relaxation effects similar to those encountered in KDA. Analogous, and even more severe, problems were encountered when similar measurements were attempted on CDA.² As an example of the problem, when the sample was cooled from several degrees above the transition to several degrees below while subjected to a field of about 2000 V/cm, the sample was incompletely polarized (approximately 75%–85% estimated saturation) as judged by electrocaloric measurements, the results of which are quite sensitive to the state of polarization of the sample. Electrocaloric measurements were successful above T_C and yielded a value for C_P consistent with the calorimetric value.

Once C_P has been estimated, it is possible to find the total entropy associated with the ferroelectric transition. The entropy recovered at temperature T is given by

$$\Delta S(T) = \frac{L}{T_C} \int_T^{T_C} \frac{\Delta C}{T} dT,$$

where L is the latent heat. The entropy change at T_C and the total entropy change associated with the transition are given in Table I.

According to the thermodynamic theory of ferroelectrics,¹⁰ the recovered entropy can be related to the polarization by

$$P^2(T) = (2/V_0\alpha)\Delta S(T),$$

where V_0 is the molar volume and α^{-1} is the Curie constant. The Curie constant and the Weiss temperature θ were obtained from dielectric constant measurements and are given in Table I. The polarization was computed from the recovered entropy and is shown in Fig. 2 on a reduced variable plot. The maximum saturation polarization at 0 K, $P(0)$, and the polarization jump at T_C , P_0 , are given in Table I.

The value of the Curie constant obtained here was approximately 8% larger than the value deter-

TABLE I. Thermodynamic properties of RDA and KDA and a comparison with predictions of the SUS theory. Symbols used are defined in the text.

Property	RDA		KDA	
	Experiment	SUS	Experiment	SUS
L/RT_C	0.280	0.322	0.377	0.376
$\Delta S(0)/R$	0.502	0.652	0.506	0.541
$P_0/P(0)$	0.745	0.753	0.862	0.866
$P(0)$ ($\mu\text{C}/\text{cm}^2$)	5.40	...	5.25	...
$1/\alpha$ (K)	223	357	187	191
θ (K)	108.0	108.7	94.25	94.74
ϵ_0/kT_C	...	0.323	...	0.360
ϵ_1/kT_C	...	3.16	...	3.92
β/kT_C	...	0.250	...	0.2057

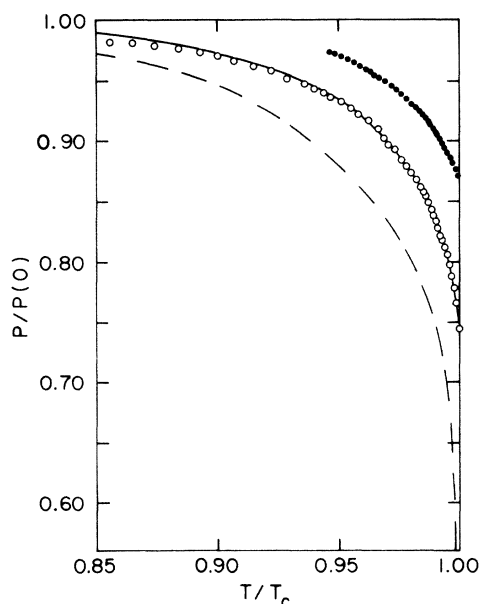


FIG. 2. Reduced polarization (polarization divided by the saturation polarization at $T=0$) as deduced from the transition entropy for KH_2AsO_4 (solid dots) and RbH_2AsO_4 (open dots). The results obtained by fitting the proton-ordering theory of Silsbee, Uehling, and Schmidt to the polarization of RDA are indicated by the solid line. The broken line indicates the reduced polarization for KH_2PO_4 .

mined by Blinc *et al.*⁴ If this latter value is adopted, the polarization values reported here would be reduced by approximately 4%.

The significant thermodynamic data for RDA (entropy, polarization, latent heat, and Curie constant) are quite consistent with those observed in other KDP-type materials when the observed trends that are associated with chemical composition are taken into account. Of particular interest is the fact that within both the phosphates and the arsenates the abruptness of the transition decreases rapidly as the atomic number of the cation increases.

II. THEORETICAL CONSIDERATIONS

The static SUS theory is a statistical treatment of possible occupation configurations of protons (or deuterons) within double minimum hydrogen bonds having assigned configuration energies of 0,

ϵ_0 , ϵ_1 , and β . Using these as adjustable parameters, we have fit the SUS theory to the polarization deduced from the entropy. In this fit, we have required that the transition occur when $T/T_c=1$ so that there are two free parameters. These two parameters can be used to adjust the polarization jump at T_c and the curvature of the polarization-vs-temperature curve, with the resulting fit shown by the solid line in Fig. 2. The fitting parameters used are given in Table I. Curves representing $P/P(0)$ vs T/T_c for KDA and KDP are included in Fig. 2.

The disagreement between the entropy and Curie constant predicted using the SUS theory and that found experimentally for RDA is similar to the situation found for KDP and CDA but not for KDA. Within the context of the hydrogen-bond-occupation model, this situation indicates that a more significant role is played by dynamic (proton-tunneling) effects¹¹ in RDA and CDA than in KDA. In general, the static SUS theory has proven to be most successful when the transition is nearly "Slater-like," i. e., when the entropy change at T_c approaches the total entropy change. Thus KDA and DKDA, which are more Slater-like than is RDA, are better described by the SUS theory than is RDA. Similarly, DKDP is more Slater-like than KDP, and the SUS theory provides a description of the thermodynamic properties of DKDP which is superior to that which it provides for KDP.

The failure of the SUS theory to account for the thermodynamic properties of those KDP isomorphs which undergo non-Slater-like ferroelectric transitions, i. e., those with greater second-order character, can be corrected by the introduction of a parameter characterizing tunneling.¹¹ However, it is not clear if this same approach will obviate yet another problem. It is possible to analyze nuclear magnetic-relaxation-time data in terms of a model based on the SUS theory.¹² This has been done for KDA and RDA, yielding values of ϵ_0/kT_c of 0.56 and 0.65, respectively. These values stand in strong contrast to those needed to account satisfactorily for the thermodynamic properties. This problem may be an indication that a different starting point, such as the lattice-dynamics approach of Kobayashi,¹³ is required for an understanding of ferroelectricity in KDP isomorphs.

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