

Evidence for Logarithmic Singularities in the Specific Heats of the Ferroelectric Crystals KH_2PO_4 and KH_2AsO_4 †

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(Received 5 April 1965)

By drawing interpolation curves between the high- and low-temperature branches of the specific heats of KH_2PO_4 and KH_2AsO_4 (measured by Stephenson and co-workers) we have decomposed each specific-heat function into the sum of a monotonic term plus an anomalous term, peaked about the transition temperature. In the region of the transition temperature θ_c we find that the paraelectric and ferroelectric branches of the anomalous specific heat of each crystal have the limiting behavior

$$C^a = -A \ln|\theta - \theta_c| + B,$$

where $A = 1.2 \pm 0.3$ cal/mole deg, $B = 0.95 \pm 0.07$ cal/mole deg for $\theta > \theta_c$, and $A = 14.2 \pm 1.4$ cal/mole deg, $B = 14.4 \pm 0.3$ cal/mole deg for $\theta < \theta_c$. These constants have the same values for both crystals.

I. INTRODUCTION

THE phenomenological theory introduced by Mueller¹ for Rochelle salt has been very successful in correlating the elastic and dielectric properties of other ferroelectric crystals. When applied to the calorimetric properties of ferroelectrics, the theory predicts that the difference in specific heats $C_E - C_D$ (where E and D refer to constant electric field and displacement, respectively) should be identically zero in the paraelectric phase, be simply related to the spontaneous polarization in the ferroelectric phase(s), and exhibit a *finite* discontinuity at the transition between the polar and nonpolar phases.²

Peaks at the transition are observed in the specific heats of a number of ferroelectrics and it is customary to interpret these peaks as being the difference $C_E - C_D$ superimposed on a smooth monotonic function viz. C_D (see Sec. III). However, in this interpretation, the specific heat in the paraelectric phase (where $C_E = C_D$) should be a monotonic increasing function of temperature and an examination of the results for a number of ferroelectrics will show³ that this is not true in the region of the transition temperature.

The specific-heat "tail," appearing in the paraelectric phase and not accounted for in the theory of Mueller, may be interpreted as due to a "smearing out" of the transition; but, for the ferroelectrics, potassium dihydrogen phosphate (KDP) and triglycine sulphate, which undergo order-disorder transitions, another explanation can be found in terms of the short-range order which contributes just such a tail to the anomalous specific heats of the ferromagnetics and the alloys.^{4,5} In view of the theoretical interest in the

behavior of the anomalous specific heat of an order-disorder system at the transition, it was thought worthwhile to analyze the primary specific-heat data of KDP⁶ and the isomorphous crystal KH_2AsO_4 .⁷

This analysis is presented in Sec. II, and in Sec. III we discuss the relationship of these results to the specific heats C_E and C_D .

II. ANALYSIS OF EXPERIMENTAL DATA

Potassium dihydrogen phosphate and potassium dihydrogen arsenate undergo ferroelectric phase transitions at 127.97 and 95.57°K, respectively. The neutron diffraction analysis of KDP⁸ has shown that the distribution of protons pass from a disordered to an ordered state as the crystal is cooled through the transition. Since KH_2AsO_4 is isomorphous with KDP with a similar ferroelectric transition, this crystal presumably also undergoes an order-disorder transition. The specific-heat curves of these two crystals, as measured by Stephenson and co-workers, have a similar appearance; that of KDP is drawn in Fig. 1.

Since the state of the electrical boundary conditions during the course of these measurements is ambiguous (see Sec. III) no firm statement about the identification of either C_E or C_D with the experimental specific heat C can be made.

An examination of the specific-heat curves of these two crystals suggests that C is of the form $C = C^o + C^a$ when C^o is a smooth monotonic function of temperature and C^a is a function sharply peaked at the transition. This separation can be made physically plausible, if not precise, if we identify C^o with the specific heat of the lattice vibrations and C^a with the specific heat of the proton distribution. If, indeed, C can be written in the form suggested above, then we should be able

Physics (North-Holland Publishing Company, Amsterdam, 1964) Vol. 4.

⁶ C. C. Stephenson and J. G. Hooley, *J. Am. Chem. Soc.* **66**, 1397 (1944).

⁷ C. C. Stephenson and A. C. Zettlemoyer, *J. Am. Chem. Soc.* **66**, 1402 (1944).

⁸ R. S. Bacon and G. E. Pease, *Proc. Roy. Soc. (London)* **A220**, 397 (1953).

† Issued as N. R. C. 8585.

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¹ H. Mueller, *Phys. Rev.* **57**, 829 (1940); **58**, 565 (1940).

² J. Grindlay, *Ferroelectricity* (Pergamon Press, Inc., New York, to be published).

³ F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

⁴ C. Domb, *Advan. Phys.* **9**, 149, 245 (1960).

⁵ C. Domb and A. R. Miedema, *Progress in Low Temperature*

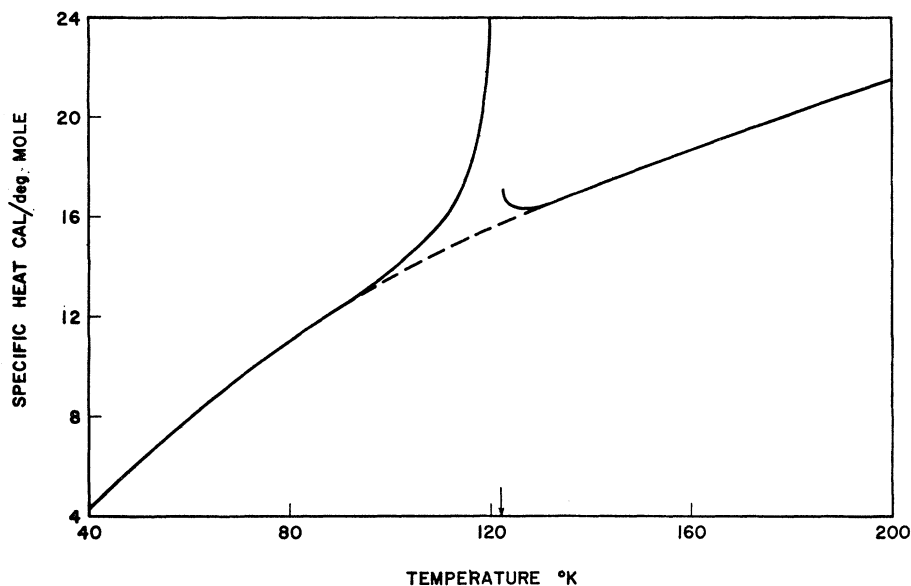


FIG. 1. The specific heat of KDP (full line) after Stephenson and Hooley. (Ref. 6) The broken line represents the interpolation curve used to obtain C^o .

to get an estimate of the values of C^o in the region of θ_c from an interpolation between the high- and low-temperature branches of C . This was done for each crystal (see, for example, Fig. 1). There is a certain amount of leeway in the choice of interpolating curve and an estimate of this led to the uncertainty flags appearing in Figs. 2 and 3.

The primary data of Stephenson and co-workers consist of a series of heat inputs ΔQ and the corresponding initial and final temperatures θ_i , θ_f . Rather than lose accuracy by using derived data, such as specific heats, we choose to analyze the behavior of C^a near θ_c by considering the anomalous heat input $\Delta Q^a = \int_{\theta_i}^{\theta_f} C^a d\theta$ which can be expressed in terms of the primary data and the interpolated values of C^o .

Since $C = C^o + C^a$,

$$\Delta Q^a = \int_{\theta_i}^{\theta_f} (C - C^o) d\theta,$$

but

$$\Delta Q = \int_{\theta_i}^{\theta_f} C d\theta,$$

and C^o is a slowly varying function of temperature; hence,

$$\Delta Q^a = \Delta Q - C^o(\theta_f - \theta_i).$$

Let us suppose that C^a has a logarithmic⁹ singularity at θ_c and write

$$C^a(\theta) = -A \ln|\theta - \theta_c| + B, \quad (1)$$

where $B = C^a(\theta_c \pm 1)$. From the definition of the anomalous heat input and this form of C^a , we get

$$\Delta Q^a = (B+A)(\theta_f - \theta_i) - A[(\theta_f - \theta_c) \ln|\theta_f - \theta_c| - (\theta_i - \theta_c) \ln|\theta_i - \theta_c|]. \quad (2)$$

⁹ Evidence for C^a of the form $A(\theta - \theta_c)^{-n}$, $0 < n < 1$, for the

Introducing the quantities

$$x = [(\theta_f - \theta_c) \ln|\theta_f - \theta_c| - (\theta_i - \theta_c) \ln|\theta_i - \theta_c|] / \Delta Q^a,$$

$$y = (\theta_f - \theta_i) / \Delta Q^a,$$

we can write Eq. (2) in the form

$$1 = (B+A)y - Ax.$$

Thus, if C^a has a logarithmic singularity of the form of Eq. (1), then a plot of y versus x should yield a straight line with intercept $1/(B+A)$ and slope $A/(B+A)$.

Plots for the data of KDP and KH_2AsO_4 above and below the transitions are presented in Figs. 2 and 3, respectively.

We wish to make the following comments about these plots:

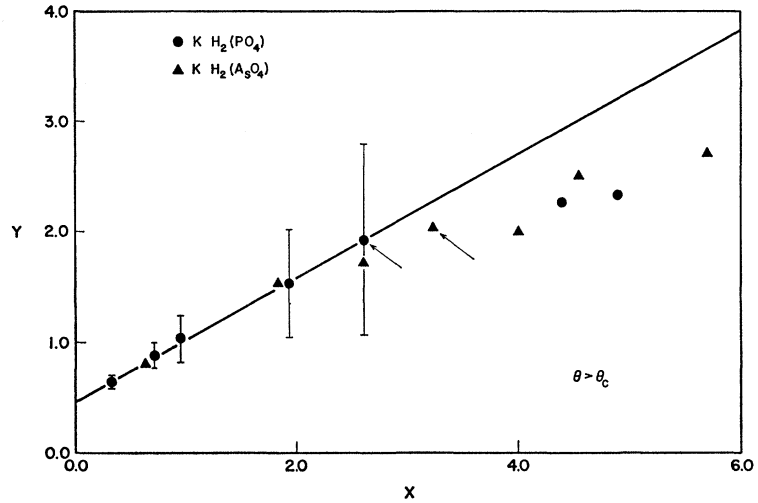
(a) The flags indicate our estimate of the uncertainty in the values of ΔQ^a due to the leeway apparent in the choice of the interpolating curves for the C^o 's. To avoid cluttered graphs we have merely put in the flags for the ordinates of the KDP points. The uncertainties in the quantities x and y are of the same order of magnitude and are similar for each crystal.

(b) The largest error in the experimental quantities arises from the uncertainty in the value of the transition temperature. This error is confined to the quantity x and is significant only within a degree of the transition. This error is sufficient to account for the scatter in the points about the straight line in the region close to the origin in Fig. (3).

(c) The pairs of temperatures of the points we have

paraelectric branches of these specific heats was sought with negative results.

FIG. 2. Plot of the quantity y versus x (see text), for KH_2PO_4 and KH_2AsO_4 in the paraelectric phase.



used lie in the range $0.6 \text{ deg} < |\theta - \theta_c| < 5.3 \text{ deg}$. It was found that points with one temperature closer than 0.6 deg to the transition point lay off the straight lines of Figs. (2) and (3) by a margin greater than one would expect from the errors discussed in (a) and (b) above. We interpret this as a reflection of the observation made by Stephenson and co-workers that, at temperatures within a degree of θ_c , complete thermal equilibrium was not achieved within the period of each measurement.

(d) The arrowed points in each figure indicate the points furthest away from the origin for which both θ_i and θ_f are within 3 deg of θ_c .

We conclude that (i) the limiting behavior of the two branches of the anomalous specific heats are of the form of Eq. (1), and (ii) the specific heats of both crystals approach the same limiting function.

The values obtained for A and B from the lines drawn

in Figs. 2 and 3 are

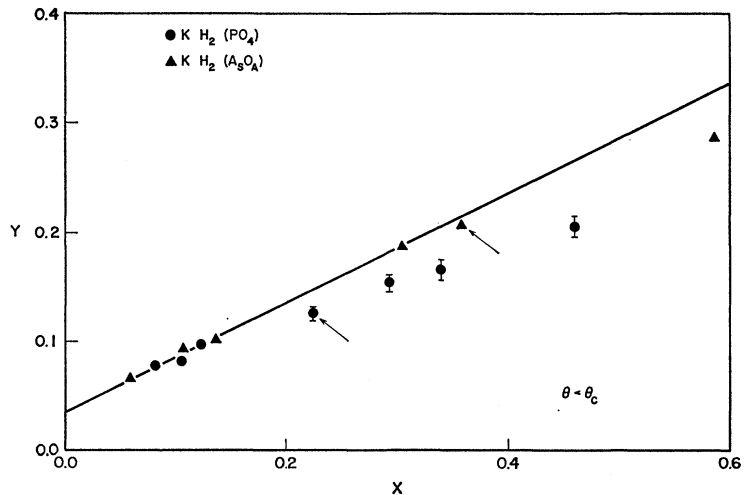
$$\begin{aligned} A &= 1.2 \pm 0.3 && \text{cal/mole deg} \\ B &= 0.95 \pm 0.07 && \text{cal/mole deg} && \theta > \theta_c, \\ A &= 14.2 \pm 1.4 && \text{cal/mole deg} \\ B &= 14.4 \pm 0.3 && \text{cal/mole deg} && \theta < \theta_c. \end{aligned}$$

The uncertainties quoted above are obtained from an estimate of the leeway in drawing the best-fitting lines.

We note that the coefficients A and B for the ferroelectric and paraelectric phases differ by an order of magnitude. This is in contrast to the case of the two-dimensional Ising model for which the logarithmic limiting behavior of the specific-heat function is symmetric about the critical point.⁴

Since $B = C^a(\theta_c \pm 1)$, the values of B quoted above should check with the slopes of the anomalous internal-energy curves at the temperatures $\theta_c \pm 1$. These curves were constructed for each crystal from the ΔQ^a data,

FIG. 3. Plot of the quantity y versus x (see text) for KH_2PO_4 and KH_2AsO_4 in the ferroelectric phase.



and in each case the B value and the corresponding slope agreed within the quoted uncertainty.

III. DISCUSSION

The results presented in the previous section indicate that the specific heats of KDP and KH_2AsO_4 , as measured by Stephenson and co-workers, possess a logarithmic singularity at the respective transition temperatures. Now a thermodynamic analysis of the properties of ferroelectric crystals shows that¹⁰:

(a) The value obtained from a specific-heat measurement on the crystal in the ferroelectric phase may depend critically on the electrical constraint and to a lesser extent on the mechanical constraints applied to the crystal.

(b) The *differences* between the specific heats for different constraints undergo at most *finite* discontinuities at the transition temperature.

We may thus conclude that evidence for a singularity in any one of the specific-heat functions of a ferroelectric can be taken as evidence for the same singularity appearing in the others. Hence, while we do not know the constraints relevant to the unplated polycrystalline specimens¹¹ used by Stephenson and

¹⁰ J. Grindlay (to be published).

¹¹ The agreement between the anomalous entropies $\int_0^\infty C_E, S^a(E=0)(d\theta/\theta) = R \ln \frac{3}{2}$

co-workers, we may still deduce that the specific heat at constant displacement (D) and constant strain (S), $C_{D,S}$, of KH_2PO_4 and of KH_2AsO_4 possesses a logarithmic singularity at the transition temperature.

In general, the specific heat $C_{D,S}$ is of interest in the comparison between theory and experiment; the present case is of particular interest since these two ferroelectrics are examples of order-disorder systems in which the dipole-dipole forces play a significant role in the phase transition.

We conclude by pointing out that a measurement of the clamped transition entropy and transition energy associated with the proton distribution requires: (a) specific-heat measurements on specimens subject to known constraints and (b) careful measurements of the dielectric properties of the ferroelectric phase. Such data are not available in the literature.

ACKNOWLEDGMENTS

We wish to thank Dr. J. A. Morrison and Dr. V. Janovec for a number of stimulating discussions.

obtained by Stephenson and co-workers and the theoretical clamped transition entropy [J. C. Slater, J. Chem. Phys. **9**, 16 (1941)] $\int_0^\infty C_E, S^a(E=0)(d\theta/\theta) = R \ln \frac{3}{2}$, associated with the proton distribution suggests that the constraint was constant (zero) electric field. The values of the anomalous entropies are 0.74 ± 0.06 cal/mole deg for KDP and 0.90 ± 0.05 cal/mole deg for KH_2AsO_4 ; $R \ln \frac{3}{2} = 0.81$ cal/mole deg.

Nonlinear and Linear Shielding of Rare-Earth Crystal-Field Interactions

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(Received 1 April 1965)

It was shown previously that significant nonlinear shielding of the rare-earth electrostatic crystalline-field interactions may occur, and hence that the standard parametrization scheme used to determine the crystal-field parameters, $V_L^M = A_L^M \langle r^L \rangle$, was questionable. These nonlinear effects arise from the same distortions of the closed shells in rare-earth ions which produce the (larger) linear shielding of the crystal field V_e . In this paper, both nonlinear and linear shielding effects have been investigated for the rare-earth ions Ce^{3+} , and Tb^{3+} through Yb^{3+} inclusive. The method of single substituted configurations is employed and is shown to avoid the difficulties associated with the traditional single-determinant perturbation-theory approach previously used exclusively by various authors. Results based on both methods are given and compared; significant differences in linear-shielding predictions are found to be introduced by the inexact traditional approach. Calculations for the nonlinear $5p \rightarrow 4f$ effects have been done, and results displayed, as a function of the strength of V_e (based on the point-charge model). The relevance of these effects to experiment is examined qualitatively.

I. INTRODUCTION

THE electrostatic crystal-field model has been used in numerous studies of the optical and magnetic properties of rare-earth ions in solids. A key role is played in these investigations by the parameters V_L^M

$= \mathcal{U}_L^M \langle r^L \rangle$ determined experimentally to represent appropriate matrix elements of the crystal-field operator

$$V_e = \sum_{L,M} A_L^M r^L Y_L^M(\theta, \varphi) \\ = \sum_{L,M} \left(\frac{4\pi}{2L+1} \right)^{1/2} \mathcal{U}_L^M r^L Y_L^M(\theta, \varphi) \quad (1)$$

* Supported by the U. S. Air Force Office of Scientific Research.

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