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Critical Phenomena in Order-Disorder Ferroelectrics. I. Calorimetric Studies of KH_2PO_4†

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High-resolution measurements of the heat capacity in the immediate neighborhood of the ferroelectric transition in KH_2PO_4 are reported. The heat-capacity anomaly is interpreted as a second-order, or nearly second-order, transition. The divergence of the heat capacity may be interpreted as logarithmic, and if so, within experimental error the divergence is symmetric in the sense that the logarithmic slopes are the same above and below the transition. If the divergence is logarithmic, little significant evidence of rounding of the heat-capacity anomaly has been found to within a few millidegrees Kelvin of the heat-capacity peak. It is also possible to interpret the data in terms of a power-law divergence, in which case the heat capacity associated with the transition behaves as $(T_p-T)^{-0.50}$ below the transition and as $(T-T_p)^{-1.0_4}$ above the transition, and the anomaly is rounded within about 0.05°K of either side of the heat-capacity maximum. The total transition entropy is found to be $(0.422\pm0.014)\,R$. Dielectric-constant measurements are also reported which may indicate that the temperature of the dielectric anomaly may be about 0.1°K lower than the temperature of the calorimetric anomaly.

I. INTRODUCTION

A CLASSICAL example of a class of ferroelectric materials which may be termed order-disorder, as opposed to displacive ferroelectrics is potassium dihydrogen phosphate (KDP). Although the transition, which is accomplished by distortion from tetragonal to orthorhombic symmetry, changes the positions of the potassium ions and phosphate groups sufficiently to account for the observed values of the spontaneous polarization, a key feature of the transition seems to be an ordering of the hydrogen-bond system.[1] The hydrogens can take either of two positions in a double minimum potential connecting phosphate groups. In the paraelectric phase there seems to be no preference between these two positions, while in the ferroelectric state the hydrogen-bond system displays long-range order with regard to which of the two positions is occupied. There appears to be a close connection between the lattice distortion, the spontaneous polarization, and the order displayed by the system of hydrogen bonds. Because of this connection, at least in a formal sense, the ferroelectric phase and the transition can be discussed solely in terms of the ordering of the hydrogen bond system.

The original model of the phase transition in KDP which spoke in terms of hydrogen ordering was put forth by Slater many years ago.[2] In this model only configurations in which two hydrogens are associated with each PO_4 group were considered because of the high energy expected to be associated with other configurations. The resulting transition was of first order, occurring at a transition entropy of $\frac{1}{2}R(\ln 2)$. The total entropy associated with the transition was found by Slater to be $R\ln\frac{3}{2}$ although recent refinements of the analysis show the value to be slightly larger.[3] If configurations other than those with only two hydrogens associated with each PO_4 group are considered, the transition can be of the second order.[4]

In addition to the evidence of hydrogen ordering gained from the neutron-diffraction studies,[5] a second consideration indicating the significant role of the hydrogens in the phase transition in KDP is the large change in transition temperature upon deuteration. The large isotope effect is taken as evidence that the tunneling of hydrogens between the two minima is a significant factor in the transition, the much higher transition temperature in the deuterated compound being associated with the much reduced tunneling probability of the deuteron. Recently, detailed theories of the ferroelectric transition in KDP have been developed which include the tunneling motion of the protons and which reduce to a theory of the Slater type in the limit of zero tunneling.[6,7] These theories can be formulated in a formal language similar to that used to describe an Ising spin-$\frac{1}{2}$ system, the exchange energy being related to energy changes in a cluster of four PO_4 groups which may be related to the positions of the hydrogen bonds existing in this cluster.[7,8] These theories are much more complex than those of the Ising type since they include the long-range, dipole-dipole terms which accompany the polarization and the kinetic energy of the tunneling motion. These theories can account for the isotope effect and can predict transitions of either the first or second

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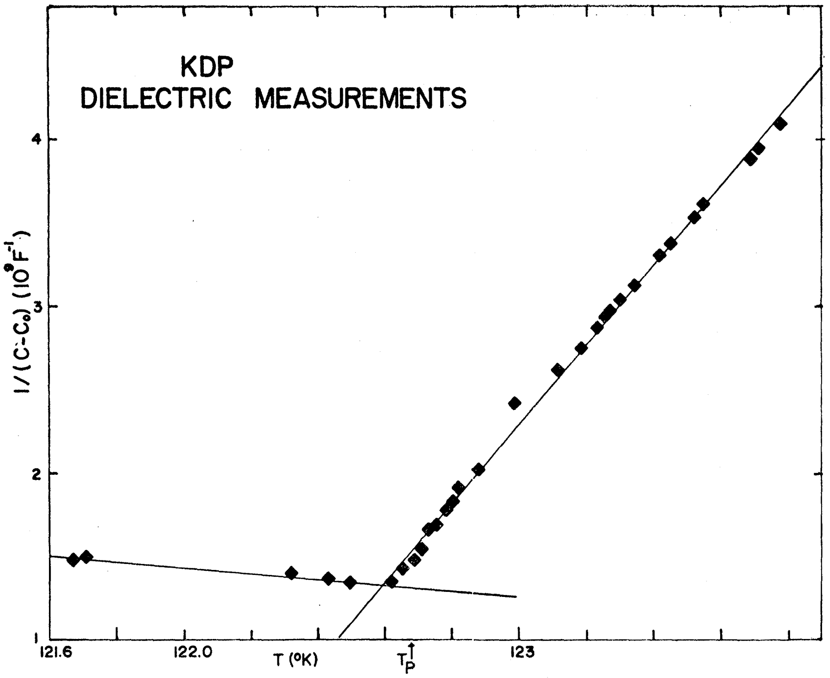

FIG. 1. The results of dielectric-constant measurements on a sample grown from the solution as those employed in the calorimetric measurements are shown in the form of a plot of the reciprocal of the measured capacity minus lead capacitance ($C-C_0$) as a function of temperature. Such a plot displays the Curie–Weiss law behavior above the dielectric maximum. The temperature of the heat-capacity maximum, T_p is shown and occurs about 0.1°K above the maximum in the dielectric constant.

order, depending on the values of certain parameters which enter the theory.

Experimentally, the transition seems to be either a diffuse, first-order or a very sharp, second-order transition. Since the transition temperature is expected to be dependent on such features as internal strains and crystal defects, first-order ferroelectric transitions are often spread over a few degrees and do not show a latent heat. In any case, the transition in KDP is quite sharp: for example, the polarization rises to about 60% of its maximum values within a few degrees of the transition.[9] The heat-capacity anomaly which accompanies the destruction of spontaneous polarization is also quite sharp and seems to be of the lambda type, showing no evidence of an isothermal absorption of heat.[10] The transition entropy seems close to the Slater values. Detailed investigations of the susceptibility and polarization in the neighborhood of the transition as functions of electric fields seem to lead to the conclusion that the parameters in the free-energy expansion are such as to indicate a second-order transition.[11] On the other hand, x-ray measurements of the spontaneous strain, a measurement which might be expected to be least affected by distributions of strains or impurities, seem to indicate that the transition is of first order, although the measurements were not carried out very near to the transition.[12] Recent measurements of the dielectric constant have been reported to show a small hysteresis (0.05°K), which is taken to indicate that the transition is of first order.[13]

Partly to try to resolve the question of the nature of the transition in KDP, and partly because, if the transition is of second order, the heat capacity should exhibit evidence of critical fluctuations, a series of calorimetric measurements in the neighborhood of the transition have been undertaken. Very small temperature intervals (roughly $\Delta T/T = 1.2\times 10^{-4}$) were used so as to reveal, as well as possible, the nature of the heat-capacity anomaly. The results indicate that the heat capacity may best be understood in terms of a second-order, or nearly second-order, transition with either a power law or logarithmic divergence of the heat capacity. If the divergence is of the power-law form then the exponent below the transition is about half that above and the heat capacity is rounded within about 0.05°K of each side of the heat-capacity maximum. If the divergence is logarithmic, it is symmetric in the sense that the logarithmic slopes are the same above and below the transition, and the transition is sharp to within a few millidegrees Kelvin of the transition. The transition entropy deduced from a combination of these results with earlier measurements are close to, but slightly larger than, $R \ln\frac{3}{2}$. The present analysis seems to indicate that the final value of the entropy is reached much more rapidly above the transition than anticipated by any of the theories of the Slater type. Further, some dielectric measurements have been undertaken which may show that the dielectric anomaly occurs about 0.1°K below the heat-capacity anomaly.

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TABLE I. A summary of the experimental data near the transition is given by averaging the data in temperature bins of varying sizes. The average temperature and average heat capacity for the points falling within the bin and the rms deviation of the data within each bin are given. The data from Series I and Series III have been treated separately.

T (°K)	C (J/mole °K)	Root mean square deviation (J/mole °K)
	SERIES I	
120.459	101	1.4
120.944	110	0.7
121.211	112	1.6
121.554	123	0.9
121.730	133	3.6
121.836	130	2.0
121.934	142	3.0
122.044	151	3.1
122.140	163	7.3
122.230	176	4.0
122.333	191	1.7
122.403	214	5.0
122.457	228	5.6
122.508	255	3.5
122.546	273	4.6
122.570	269	12.6
122.592	290	7.5
122.615	318	3.3
122.638	334	11.1
122.656	336	7.5
122.676	432	8.1
122.683	505	10.2
122.695	371	5.8
122.719	243	8.3
122.747	191	6.1
122.776	174	9.2
122.817	133	4.5
122.859	111	3.1
122.909	102	4.7
122.963	92.0	2.9
123.035	87.8	4.5
123.115	82.3	0.1
123.236	73.8	2.1
123.343	75.0	2.1
123.433	77.4	2.0
123.687	74.5	0.3
124.199	80.9	8.2
	SERIES III	
122.365	195	4.4
122.477	229	7.9
122.533	260	6.4
122.558	283	9.6
122.584	291	5.1
122.594	311	6.2
122.604	281	12.4
122.617	340	7.6
122.625	350	...
122.634	350	12.6
122.644	364	2.9
122.654	392	15.3
122.662	394	17.5
122.675	458	8.9
122.684	450	6.8
122.692	375	7.8
122.698	296	14.0
122.704	264	14.2
122.714	233	10.4
122.723	230	14.4
122.738	182	4.3
122.758	155	3.7
122.825	118	...

II. EXPERIMENTAL

The samples employed in the calorimetric measurements were small single crystals (typically from 10 to 50 mm^3) grown from an aqueous solution prepared using reagent grade KDP. The crystals were placed in a copper cylinder 6.35 cm long with 1.42 cm i.d. which was fitted with a screw cap which made a vacuum seal using an indium O ring. The sample (9.872 g in Series I, 9.969 g in Series III) was loaded in the cylinder with 1.867×10^{-4} moles of He gas which was used as a heat-exchange medium.

The cylinder was rigidly hung inside an adiabatic shield using six nylon strings each 0.015-cm diam by 4.5-cm long. The shield was mounted within a vacuum can, sealed with an indium O ring, on a $\frac{1}{2}$-in. o.d. by 0.01-in. wall stainless-steel tube 8.5 cm long. The vacuum can was immersed in liquid nitrogen to provide cooling through the stainless-steel support rod. For initial cooling gaseous helium was used as a heat-exchange gas, but this was pumped to a pressure of less than 5×10^{-7} Torr before measurements were begun.

One junction of a 0.002-in.-diam–chromel-alumel, differential thermocouple was mounted on the sample container with the other junction being on the shield. The thermocouple voltage was measured with a Kiethly Model 149 millimicrovoltmeter, the output of which was employed as the error signal in a simple one-transistor current-control circuit which drove the shield heater. Using this circuit, the rms temperature difference between the shield and sample was less than 3 m°K except when heat was being added to the sample. During heating periods, the shield-sample temperature difference was about 60 m°K. The sample-shield thermal resistance, about 2×10^{-4}W/°K, primarily radiation resistance, was such that heat loss to the shield while heating was at most 0.1% of the heat which was supplied and during the process of equilibration (taking less than 20 min) less than 0.1% of the total heat added to produce a temperature step could be lost to the shield. After suitable precautions concerning the optical and thermal shielding of power carrying leads, long-term temperature stability in the calorimeter was such that a drift of less than 0.01°K occurred during 20 h.

Measurements were taken using the conventional, discontinuous heating technique. The heat was supplied electrically to a bifilar manganin heater with a total resistance of 100 Ω which was wound about the sample container and cemented in place with GE 7031 varnish. The power dissipated in the heater was determined by four-terminal potentiometric measurements using a L & N Type K-3 potentiometer. The time duration of the heat application was determined using an Anadex Model CF200 Counter-Timer which was gated on and off by an electrical signal coupled to the heating circuit. The accuracy of the determination of the amount of heat supplied, about 0.01%, was not a limiting con-

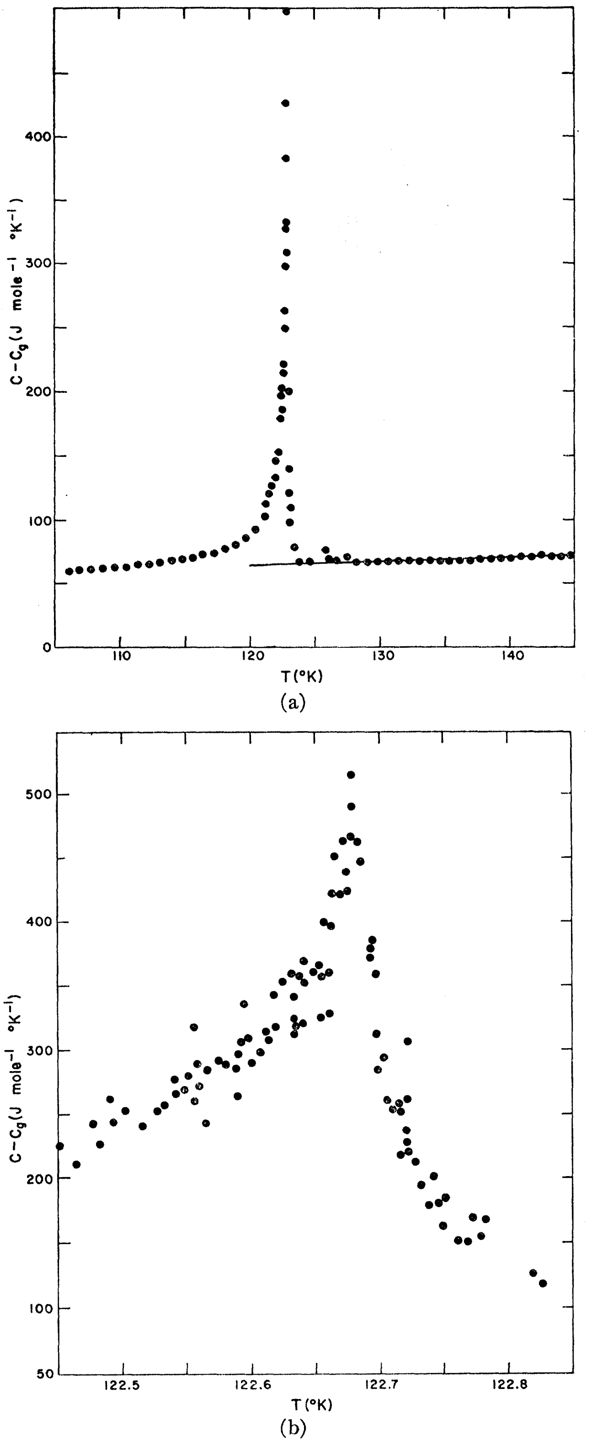


FIG. 2. The heat capacity of KDP. With the exception of the points in the immediate neighborhood of the transition the points shown in Fig. 2(a) were taken with temperature intervals of approximately 1°K. The points shown in Fig. 2(b) were taken with smaller intervals, typically between 0.05°K and 0.014°K. The points shown in Fig. 2(a) were taken from Series I, those shown in Fig. 2(b) were taken from both Series I and Series III. Note the change in origin between Fig. 2(a) and Fig. 2(b). The solid line in Fig. 2(a) shows the expression chosen to represent C_G, the lattice heat capacity.

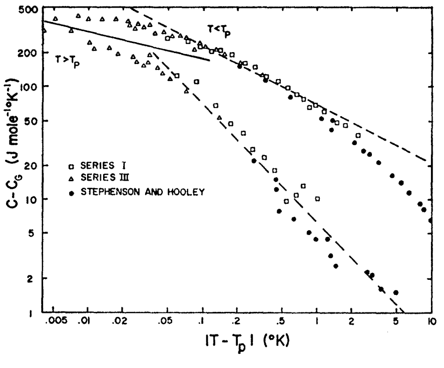
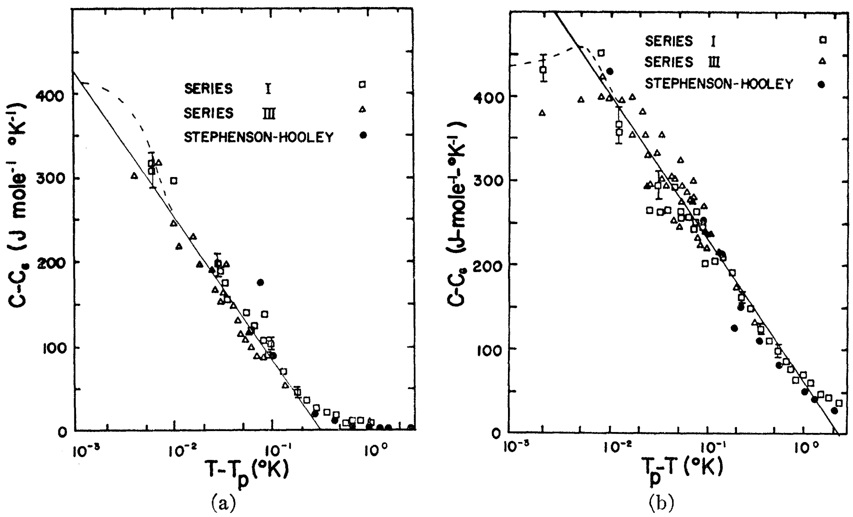


FIG. 3. A log-log plot of C-C_G versus $|T-T_p|$. The points shown for $|T-T_p|>0.04°$ are averages of several points while those closer are individual points from Series III. The points labeled Stephenson and Hooley are taken from Ref. 10 and are used to represent their work in the region $|T-T_p|>0.2$, both to demonstrate agreement between the two sets of experiments and to provide a basis for extending the results of the current investigation to larger values of $|T-T_p|$. Other data from Ref. 10 have not been plotted so as to aid legibility. The solid line merely divides the points above and below T_p. The dashed lines represent attempts to fit the heat capacity data to expressions of the type $C-C_G\propto|T-T_p|^{-\alpha}$ in the region $1\geq|T-T_p|\geq0.05$ and give as results $\alpha=1.0_4$ above T_p and $\alpha=0.50$ below T_p.

sideration on the accuracy of the experiment, being much less than the uncertainty arising either from determination of the temperature change or the uncertainty arising from heat lost to the shield.

The most difficult aspect of calorimetry employing small changes in temperature is to determine the temperature change with sufficient accuracy. To this end one needs sensitive thermometer and sensitive detecting instrumentation. As a thermometer element a low-temperature thermistor (Keystone Carbon Co. Type RL10X04) was chosen which had a temperature coefficient of approximately 100 Ω/°K in the vicinity of the heat-capacity maximum. The thermistor was potted with a thin coat of Epibond 104 Epoxy resin in an effort to insure the stability of the calibration of the thermistor. During the course of several months of use, involving many cyclings between room temperature and 100°K, a shift of about 0.016°K in the calibration of the thermometer occurred. This shift did not seem to be associated with the cyclings, but rather occurred when the thermistor stood at room temperature for a period of about a month, and was probably associated with a small amount of moisture penetrating the potting.

The thermistor was calibrated against a Platinum-resistance thermometer (L & N Type 8164) calibrated locally according to the International Practical Temperature Scale. In the future, when scheduling problems at the National Bureau of Standards are overcome, the thermometer will be calibrated at NBS. This may cause a shift in the absolute values of the temperatures involved, but should not cause much change in the size of the degree employed in this work. As we are more interested in temperature differences than actual



(a) (b)

FIG. 4. The heat capacity associated with the ferroelectric transition, $C-C_G$, is shown plotted against the logarithm of the difference in temperature between the center temperature of the experimental point and the peak temperature, T_p. Figure 4(a) shows points above T_p while Fig. 4(b) shows points below T_p. The points shown for $|T-T_p|>0.1°$ are averages of several points. The peak temperature has been chosen to give equal logarithmic slopes above and below T_p. The solid lines are best fits to the expression $C-C_G=A+B\log|T-T_p|$. The dashed lines show the effect of employing finite temperature steps under the assumption of a logarithmic divergence in the heat capacity. The solid circles give data taken from Ref. 10. The points of Ref. 10 shown at $T-T_p=0.08$, -0.01, and -0.19 were taken using temperature intervals which crossed the peak in the heat capacity and should not be directly compared with the other points, but are included for reference.

temperatures, any changes arising from recalibration should not be significant concerning the main conclusions of this work.

The thermistor resistance was measured using a 37-Hz Wheatstone bridge of local design which employs lock-in detection. The power dissipated in the thermistor was less than 7 nW, contributing negligibly to the heat leak to the sample. During Series I one could determine the resistance with a precision of approximately 0.03 Ω so the temperature precision was approximately 0.3 m°K. For Series III, the bridge sensitivity was improved so that the precision was approximately 0.005 Ω and the resulting temperature precision was about 50 μ°K. Temperature changes could be determined with a precision of about 200 μ°K, half the uncertainty coming from the determination of each end temperature and half coming in the ability to judge equilibrium. Thus the temperature difference for the smaller steps, about 0.014°K, could be determined to about 8.5% during Series I and 1.5% during Series III. Away from the peak slightly larger steps were taken, but because of the increasing importance of the addenda correction, the accuracy of the measurements was roughly constant over the entire range. The over-all precision of the heat-capacity measurements was then 10% during Series I and 2% during Series III when proper account is taken of all factors including the addenda correction. During Series I, some of the increments were twice as large as the increments mentioned above. During Series I two sets of measurements were carried out over the range from 105 to 145°K using larger temperature increments, about 1°K. The addenda heat capacity was measured in a separate series of measurements and agreed well with the value calculated from the known mass and composition of the addenda.

In addition to the calorimetric measurements, some measurements were made of the dielectric constant of KDP near the ferroelectric transition using a sample grown from the same solution as the calorimetric samples and employing the same thermometry as was used in the calorimetric experiment. The sample was a flat plate 0.71×0.50×0.15 cm cut from a large single crystal. After water-polishing to remove the strains induced by cutting, silver paint plates were attached perpendicular to the ferroelectric axis. The sample was mounted in intimate thermal contact with the thermometer in the calorimeter. Measurements of the dielectric constant as a function of temperature were made using a General Radio Type 716 Capacitance Bridge operating at 1 kHz and employing a peak field of 30 V/cm. Measurements were generally taken between heating steps, for under these conditions better temperature stability obtained than when a cooling period was allowed between measurements. We observed no hysteresis in the dielectric measurements, although our equipment was not as sensitive as that employed by Craig.[13] The results of our measurements are presented in Fig. 1 in which the reciprocal of the measured capacitance C, corrected for lead capacitance C_0, is plotted against temperature to display Curie-law behavior above the transition and a nearly temperature-independent dielectric constant below. The crossing of the high- and low-temperature behavior occurs at 122.58°K, approximately 0.1°K below the temperature of the heat-capacity anomaly.

To test for shifts in the thermometer, a series of heat-capacity measurements was carried out immediately at the conclusion of the dielectric-constant measurements (Series II). In this series, the dielectric sample and the rest of the crystal from which it was cut formed 18.5% of the sample, the rest of the sample being crystals from Series I. No difference in the position of the heat-capacity peak from that found in the other Series was noted, although in this case the transition was broadened considerably. This may be due to a broadening of the transition in the crystal from which the dielectric sample was cut caused by the presence of strains induced by the cutting or because of different transition temperatures between the dielectric crystal and the small crystals employed as samples in the other measurements.

A difference between the temperatures of calorimetric and dielectric anomalies is certainly unexpected on the basis of previous results, and the validity of this effect will be tested more extensively in the near future. If the result is correct, it may indicate the transition to be of first order and, in any case, indicates that care should be taken in the interpretation of data between 122.58°K and T_p.

III. RESULTS AND DISCUSSION

The results of the calorimetric measurements are summarized in Table I and shown in Fig. 2, in which the heat capacity is plotted as a function of temperature on scales with differing resolution about the peak. The points shown are but a portion of over 500 data points taken during this investigation and were selected to give coverage to the ranges shown. Except in the immediate neighborhood of the heat capacity peak, the points shown in Fig. 2(a) were obtained using temperature increments of approximately 1°K while those shown in Fig. 2(b) were taken with much smaller intervals, typically from 50 to 14 m°K. The solid line in Fig. 2(a) is a best fit of the data above 130°K to the expression

$$C_G = 21.43 + 0.3466T \text{ (J mole}^{-1}\text{ °K}^{-1}\text{)}, \qquad (1)$$

which is taken to represent the lattice heat capacity in this temperature region. This, of course, is a working hypothesis concerning a point which is not accessible to experimental verification. The correctness or incorrectness of this hypothesis may effect some of the conclusions reached in later analysis of the data. In particular, the temperature dependence of the heat capacity excess above the lattice contribution will be strongly affected by this choice in the region above T_p in which it is small. This choice also will affect to a lesser extent the calculation of the transition entropy and will lead to the conclusion of an unexpectedly rapid disappearance of short-range order above the transition.

The data in the immediate neighborhood of the heat-capacity peak have been replotted in Fig. 3 where the logarithm of the excess heat capacity associated with the ferroelectric transition, $C - C_G$, is plotted against the logarithm of the difference between the peak temperature T_p and the temperature of the heat-capacity point, which was taken to be half way between the initial and final temperatures of the point. The data for temperatures further than 0.04°K from T_p have been averaged over intervals of varying sizes, the interval size being chosen so that little difference in heat capacity occurs across the interval. The lattice contribution was obtained from Eq. (1).

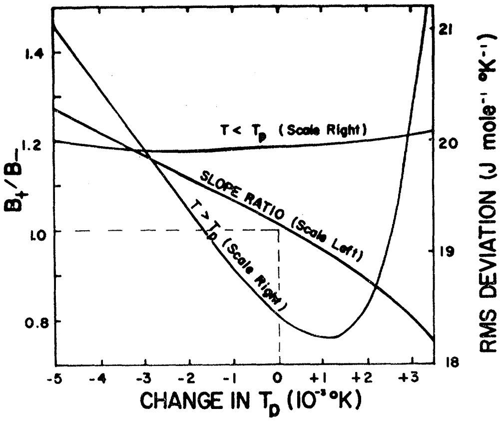


FIG. 5. The results of changing the peak temperature on the resulting ratio of logarithmic slopes and rms deviations of the data from the fitted expressions are shown. The dashed lines indicate that the chosen peak temperature was such as to give nearly equal slopes. The slight change in the combined deviation which could be obtained by moving T_p about 1 m°K in either direction about the value chosen is not considered experimentally significant. The resulting slope ratio is then $B_+/B_- = 1.00 \pm 0.05$.

Some results taken from the earlier work of Stephenson and Hooley[10] are also indicated in Fig. 3. In the analysis of their data, their value of 121.97°K for the peak temperature was taken, and the lattice contribution was calculated in a different way from that used for our data. Here the lattice contribution was determined by fitting all of their data between 16 and 300°K, with the exception of that between 83 and 140°K (the region within which the effects of the transition occurred), with an eight parameter fit employing orthogonal polynomials. In the region above 120°K there was negligible difference between this result and Eq. (1). As a test, the fit agreed well with the experimental data between 130 and 140°K, indicating that in this region the fit was a good basis for extrapolation and that there seems to be negligible excess heat capacity in this region. The resulting polynomial was then used to represent C_G. This polynomial was used to calculate the excess heat capacity both for presentation in Fig. 3 and for the calculation of the transition entropy. This choice for C_G has the same uncertainties accompanying its choice as did the former. It is comforting, however, that this independent method leads to agreement with one of the assumptions of the former choice.

The presentation of the data given in Fig. 3 attempts to fit the data to an expression of the form

$$C - C_G \propto |T - T_p|^{-\alpha},$$

where the exponent may have differing values above and below T_p. The data, at least below T_p, do not seem

Table II. A comparison of the spontaneous polarization as calculated from the heat-capacity jump with the experimental results of von Arx and Bantle.

T_p-T (°K)	P_s (10^{-6} C/cm^2)	Calculated from Eq. (2) (10^{-6} C/cm^2)
0.03	0.92	0.60
0.08	1.59	1.16
0.13	1.79	1.49
0.48	2.50	2.64

to fit such an expression well over the full range, and in both cases deviations occur for $|T-T_p|<0.05°$. If one assumes that a power law divergence is the correct interpretation of the data, this latter deviation is taken as the effect of the rounding of the transition, perhaps due to crystal imperfections. In Fig. 3, we have attempted to fit the data in the region $1°\geq|T-T_p|\geq 0.05°$ and find as the resulting values for the exponent $\alpha=1.0_4$ for $T>T_p$ and $\alpha=0.50$ for $T<T_p$. These values for the exponent are larger than the values of critical exponents obtained in most experiments on other substances and substantially larger than those indicated by any of the current theories of critical-point phenomena.[14] Further, the result that the exponent obtained above the transition is almost twice that obtained below is in conflict with the scaling-law result that the exponents should be equal.[14]

An alternative way of explaining the curvature exhibited by the data in Fig. 3 is to assume that the divergence is logarithmic rather than given by a power law. This hypothesis has been tested by the presentation of the data given in Fig. 4 in which $C-C_G$ is plotted versus $\log|T-T_p|$.

As the agreement of the data with the assumed form extends to much smaller values of $|T-T_p|$ for this case than in the case of the power-law analysis, the proper choice of T_p is much more important than in the previous case. There is considerable difficulty in the choice of the proper temperature to be used for T_p since the experimental data may be expected to display rounding because of crystal imperfections, strains, and the effect of the finite temperature steps employed. The data were analyzed to select the best value of T_p by considering only those data outside the region of possible rounding, namely, those points which display a strong temperature dependence. This involved ignoring data in a region of about 0.02°K around T_p. The remaining data were then fit in the sense of least squares to the expression

$$C-C_G=A_\pm+B_\pm\log|T-T_p|,$$

where the subscript indicates temperatures above (+) or below (−) the peak and logarithms are taken to the base 10. These fits were calculated for values of T_p taken every 0.5 m°K in the region within which the peak might be located. The rms deviation between the data and the logarithmic fit were calculated for each value of T_p. The results of these calculations are shown in Fig. 5 in which the ratio of logarithmic slopes, B_+/B_-, and the rms deviations to the fits are presented as functions of the change in the peak temperature from that finally adopted (122.687°K). The best fit to the data above T_p was obtained with a temperature about 1 m°K above that chosen, and the best fit to the data below T_p was obtained about 2.5 m°K below that chosen, so the value chosen is a compromise taken about 0.5 m°K below the minimum in the combined deviation. It is felt that any improvement obtained by moving the peak temperature by about 1 m°K in either direction about the point chosen is not experimentally significant. The point chosen gives a value of about 1 for the ratio of slopes but in view of the uncertainty in locating T_p we can at best limit the slope ratio to 1 ± 0.05.

Also shown in Fig. 4 is an indication of the rounding which is to be expected in the experimental data due to the use of finite temperature steps. This effect is indicated by the broken line which was calculated under the assumption that the heat capacity fit the logarithmic divergence exactly and that the temperature interval employed was 14 m°K, typical of those actually used. The data display at most little rounding which can not be accounted for by the effect of finite temperature steps, at least to within a few millidegrees Kelvin of the peak.

The resulting logarithmic fits to the present results gave

$$C_+=-86.7-171\log(T-122.687)\text{ J/mole }-°\text{K}$$

above the peak and

$$C_-=61.0-170\log(122.687-T)\text{ J/mole }-°\text{K}$$

below the peak. These expressions fit the data quite well in the region from T_p-1°K to $T_p+0.2$°K. The result above T_p is considerably different from that obtained by Grindley[15] who attempted to fit the Stephenson-Hooley data in the region beyond 0.6°K from T_p. The logarithmic slope obtained below T_p agrees with that obtained in Grindley's analysis. If one is to accept the above analysis as the best representation of the data, this implies that the transition can be understood as a logarithmic divergence with a discontinuity at the transition. In the sense that $B_+=B_-$, the transition would seem similar to that found for the two-dimensional Ising model[16] and the transition λ in liquid helium.[17]

Assuming a logarithmic divergence, the critical region encountered in KDP, as evidenced by the region of fit to the assumed divergence, is considerably more

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[14] L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967).

[15] J. Grindlay, Phys. Rev. **139**, A1603 (1965).

[16] L. Onsager, Phys. Rev. **65**, 117 (1944).

[17] See M. J. Buckingham and W. M. Fairbank, *Progress in Low Temperature Physics 3*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), p. 80.

narrow than other cases previously investigated.[17–20] This may be taken to be an indication that long-range (dipole-dipole) forces are important in the transition, since it is expected that the critical region will extend over a temperature region related to T_p/z, where z is the number of interaction partners.[21]

As is often the case, the present data can be interpreted as giving comfort to either the adherents of a power-law divergence or of a logarithmic divergence. However, we feel that the logarithmic divergence is perhaps the favored interpretation of the present data. Chiefly this conclusion comes from the fact that it would appear quite unlikely for the "rounding" of the transition which occurs for $|T-T_p|<0.05°$ in the power-law analysis to obey a logarithmic divergence as well as the present data appear to do. Further, because of the long-range nature of the forces involved in the ferroelectric transition, one expects critical point phenomena to be restricted to the region very near T_p, while the region of a power-law fit is best in a more distant region than the region of logarithmic fit. It can be observed that the region of fit to the logarithmic fit is slightly greater than that to the power-law fit in the case $T<T_p$ while the two types of analysis give rather similar ranges of fit above the transition, although this observation probably has little relevance. In any case, the logarithmic fit gives a very good *representation* of the experimental data, and so it will be used in the further analysis of the data.

The jump in the heat capacity ΔC is associated with the energy involved in the destruction of polarization and should be given by an expression of the type

$$\Delta C = A_- - A_+ = \tfrac{1}{2} f (dP_s^2/dT)\,|_{T_p},$$

where f is the Lorentz factor and P_s the spontaneous polarization. If we assume that the derivative is approximately constant in the neighborhood of the transition, we obtain

$$P_s(T) = [(2\Delta C/f)(T_p - T)]^{1/2}. \tag{2}$$

Following von Arx and Bantle[9] we take $f=0.33$ and compare the predictions of Eq. (2) with their experimental results in Table II. Since the experimental values are taken from a plot with a rather coarse scale, there is considerable uncertainty in the values of T_p-T; however, there is at least qualitative agreement between the calculated and experimental values. Beyond $T_p-T=0.5$°K, the experimental values rise less rapidly than do the calculated results, indicating that the assumption of a constant derivative breaks down in this region. There is some indication that very near the transition the polarization rises faster than predicted by Eq. (2), so critical phenomena may well be important in the polarization; however, these data have the largest uncertainty in the determination of T_p-T, which may account for the discrepancy.

An alternative explanation of the heat-capacity anomaly might be that the transition, rather than a second-order transition, is of the first-order, but spread over a range of temperatures by such effects as a distribution of strains or by interphase energy. A quantitative test of the first explanation is rather difficult, although, under most reasonable assumptions, one might be led to expect a broad distribution of strains, and hence a broader transition than that observed here, perhaps of Gaussian shape. Further, any such explanation might encounter difficulty in accounting for the fact that there is significant excess heat capacity, as much as 5°K above the heat-capacity peak, since the shift in transition from a completely free to a clamped crystal is only about 4°K.[22]

A quantitative test of the idea that the transition is of first-order broadened by the effects of interphase energy terms is possible, since such a theory has been worked out in detail (and applied to KDP).[23] In this theory, two empirical parameters enter, the transition entropy and the interphase free energy which picks the peak height. This calculation gives an anomaly which is symmetric about the peak, a feature that this transition does not display. However, the asymmetry could be ascribed to terms involving the temperature dependence of the spontaneous polarization in the ferroelectric regions. So as not to rely on the asymmetry, we have attempted to analyze the data in a manner most favorable to the two-phase theory; namely, by trying to fit only that portion above the heat-capacity peak. The transition entropy was chosen as twice that occurring above the peak, while the interphase free-energy parameter was chosen to be the value required to match the peak height. This choice, 4900 cal/mole, seems rather high, being approximately 25 times the domain-wall energy in KDP,[24] although one would suspect that the paraelectric-ferroelectric boundary should involve less, rather than much more, strain energy than the boundary between two ferroelectric domains. Even under these conditions, which have been chosen as most favorable to the two-phase theory, the calculation fails to match the experimental results even remotely. The calculation falls below the experimental results above $T_p+0.3$°K and rises to almost its full height in the

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[18] M. I. Bagatskii, A. V. Voronel, and V. G. Gusak, Zh. Eksperim. i Teor. Fiz. **43**, 728 (1962) [English transl.: Soviet Phys.—JETP **16**, 517 (1963)]; A. V. Voronel, Yu R. Chashkin, V. A. Popov, and V. G. Simkin, Zh. Eksperim. i Teor. Fiz. **45**, 828 (1963) [English transl.: Soviet Phys.—JETP **18**, 568 (1964)].

[19] J. Skalyo, Jr., and S. A. Friedberg, Phys. Rev. Letters **13**, 133 (1964).

[20] D. T. Teaney, Phys. Rev. Letters **14**, 898 (1965).

[21] R. Brout, *Phase Transitions* (W. A. Benjamin, Inc., New York, 1964), Chap. 2. For a more sophisticated form of this argument, leading to much the same conclusion see: V. L. Ginzburg, Fiz. Tver. Tela **2**, 2031 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1824 (1960)].

[22] H. Baumgartner, Helv. Phys. Acta. **24**, 326 (1951).

[23] A. V. Tobolsky, J. J. Kozak, and N. H. Canter, Phys. Rev. **138**, A651 (1965).

[24] W. Kanzig and R. Sommerhalder, Helv. Phys. Acta. **26**, 603 (1953).

region between 0.1 and 0.05°K and above T_p. At the worst point, about 0.075°K above T_p, the theoretical value is about a factor of 2.5 higher than the experimental value. All other assumptions about the parameters of the theory lead to even poorer fits. Thus, this two-phase theory does not give a good account of the experimental data and is rejected in favor of the hypothesis of a second-order transition.

The transition entropy was calculated from a combination of the current results near T_p and the results of Stephenson and Hooley outside the immediate neighborhood of the heat-capacity peak. The entropy change between T_p-1°K and $T_p+0.2$°K was calculated from the logarithmic fits under the assumption of no rounding of the transition. The errors were assigned on the basis that the transition rounded 10 m°K below and 3 m°K above T_p. The data outside the logarithmic region were integrated graphically. This was done since the logarthmic fits gave a good representation of the experimental data, at least to the region indicated above by the setting of the error limits. The results of this calculation were that for the entire transition an entropy change was $(0.422\pm0.014)R$, while the entropy change below T_p was found to be $(0.405\pm0.0135)R$. The result for the total transition entropy is slightly larger than $R\ln\frac{3}{2}$, and, in fact, a larger value *must* be expected if the transition is to be of second-order, for in that case it is crucial that configurations other than those with exactly two hydrogens per phosphate group be included if the transition is not to be of first order. Since the correct parameters for the application of such theories are not known with certainty, it is not clear if the value of the transition entropy as currently determined is sufficiently large to allow the transition to be of second order.[25] In this context one might also note that the present results differ from the predictions of all theories of the Slater type in that the destruction of short-range order takes place in a narrow temperature range above the transition rather than being spread over a broad temperature range. This may imply that our choice of C_G is somewhat too large and that, in fact, the total transition entropy is somewhat larger than the value deduced above (although such a change in C_G will make only a small change in the entropy change from 0°K to T_p).

In conclusion, we find that on the basis of the calorimetric evidence the transition in KDP can be understood in terms of a second-order transition (or perhaps a first-order transition with very small latent heat) since critical-point phenomena seem important, although the transition entropy, while in good agreement with the idea that the ferroelectric transition can be associated with an ordering of the hydrogen-bond system, may be slightly too small to allow a second-order transition according to current theories. The heat-capacity peak can be analyzed either in terms of a power law or a logarithmic divergence, although the authors feel that the logarithmic divergence may be the best representation of the critical behavior in the present case. If the logarithmic divergence is the correct representation, we find that the divergence is symmetric in the sense that the logarithmic slopes are, within experimental error, the same above and below the transition.

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[25] Employing the notation of Ref. 4, we find that the present value of the transition entropy could be consistent with a second-order transition if $\epsilon_1/k\geq1100$ and β/k is ≤ 12.

Erratum

Isomer Shift of Fe^{57} in Iron, R. Ingalls [Phys. Rev. **155,** 157 (1967)]. The units in Eq. (3), line 1, should read mm/sec instead of cm/sec. The expression on p. 158, Col. 2, line 16, should read $\psi_d(\mathbf{r})=Y_{lm}(\theta,\phi)u(r)/r$ instead of $\psi_d(\mathbf{r})=Y_{lm}(\theta,\phi)ru(r)$. The constant β has units of a_0^{-2} in Eq. (8). The u^2 functions have units of a_0^{-1} instead of a_0^{-3} in Eqs. (18), (19), (26), and (30), and also in Figs. 3, 5, 6, and 8.