

Studies of Phase Transitions in Order-Disorder Ferroelectrics. III. The Phase Transition in KH_2PO_4 and a Comparison with KD_2PO_4

W. REESE

Department of Physics, Naval Postgraduate School, Monterey, California

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Calorimetric, dielectric, and electrocaloric measurements have been performed on single-crystal samples of KH_2PO_4 in the neighborhood of the ferroelectric phase transition, and show that the transition is of first order, with a discontinuous entropy change of $(0.0456 \pm 0.0059 \pm 0.0045)R$ and a change in the dielectric constant by a factor of 2. Calorimetric measurements in applied electric fields were also carried out, and show that the effect of an applied field is to shift the transition to higher temperatures and to broaden it. Calorimetric measurements on KD_2PO_4 are reported which can be combined with previously reported results to give the heat capacity for this material in the range 80–280°K. Comparison of the heat capacity of KH_2PO_4 and its deuterated isomorph allows estimates of the lattice heat capacity to be made. From this estimate, the entropy change associated with the ferroelectric transition is found to be $(0.400 \pm 0.036)R$ for KH_2PO_4 and $(0.457 \pm 0.034)R$ for KD_2PO_4 . A significant feature of the comparison is the lack of evidence for the heat-capacity contribution above the transition predicted by theories of the Slater type. Comparison of the calorimetric data with the modified Slater theory due to Silsbee, Uehling, and Schmidt shows that this theory describes KD_2PO_4 better than it does KH_2PO_4 . The differences between the theory and experiment are of the type predicted by the modifications of the theory which include tunneling motion of the protons.

I. INTRODUCTION

PREVIOUS investigations of the heat capacity of KH_2PO_4 (KDP) in the neighborhood of the ferroelectric transition seemed to indicate that the transition was of second order,^{1,2} although hysteresis has been reported in measurements of the dielectric constant, which indicates a transition of the first order.³ Recently, it was found that the transition in the deuterated isomorph KD_2PO_4 (DKDP) was of first order.⁴ On the basis of these observations it seemed of interest to undertake a reinvestigation of the transition in KDP using a single-crystal sample, since the previous calorimetric investigations employed samples consisting of many small crystals with ill-defined electrical boundary conditions.

One result of this reinvestigation was to find that the transition, when examined with a single-crystal sample, was of first order. In addition, an investigation was made into the effects of applied electric fields, which were found to broaden the transition and shift it to higher temperatures. The latent heat appears to go to zero for fields in excess of about 300 V/cm.

A series of dielectric measurements was made simultaneously with calorimetric measurements. The temperature of the dielectric and calorimetric anomalies was found to be the same, although this fact was somewhat obscured by a broadening of the transition when plated electrodes were present. The dielectric constant is found to change discontinuously by a factor of approximately 2 between the paraelectric and ferroelectric state.

Measurements of the electrocaloric effect were made which substantiate the interpretation of the calori-

metric and dielectric measurements. These measurements also point out that nonlinearities in the field dependence of the polarization manifest themselves at quite low values of the applied field near the transition.

An extensive series of calorimetric measurements on DKDP between 80 and 280°K is also reported. A comparison of the heat capacities of KDP and DKDP was made, which forms the basis for an estimate of the lattice heat capacity. The most striking feature of this comparison is that there exists scant evidence for a nonlattice-heat-capacity contribution extending more than about 20° above the transition. This feature is in direct contrast to the predictions of that class of theories of the ferroelectric transition in KDP-type materials which places main emphasis on the ordering of the protons in the possible H-bond positions. The entropy associated with the destruction of the spontaneous polarization was calculated, and a slightly greater entropy change was found by DKDP than for KDP. An analysis of the behavior of the heat capacity in the immediate vicinity of the ferroelectric transition of KDP was made. It was found that in the neighborhood of $\epsilon = (T_c - T)/T_c = 2 \times 10^{-4}$ the heat capacity goes from a $1/\sqrt{\epsilon}$ to a $\log \epsilon$ dependence.

In the previous papers in this series^{2,4} some discussion of the theoretical interpretation of the ferroelectric transition in KDP-type ferroelectrics has been given, so such discussion will be omitted here. The emphasis of this paper will be on the nature and limitations of the empirical results. After a brief discussion of experimental details in Sec. II, the nature of the phase transition in KDP and the phenomena occurring at this point will be explored in Sec. III, where the evidence which shows the transition to be of first order will be presented, and an investigation of some thermodynamic aspects of the transition will be made. Data concerning the effects of electric fields on the heat capacity will also be presented. In Sec. IV, the heat capacity of

¹ C. C. Stephenson and J. G. Hooley, *J. Am. Chem. Soc.* **66**, 1397 (1944).

² W. Reese and L. F. May, *Phys. Rev.* **162**, 510 (1967).

³ P. P. Craig, *Phys. Letters* **20**, 140 (1966).

⁴ W. Reese and L. F. May, *Phys. Rev.* **167**, 504 (1968).

DKDP will be discussed, a separation of the heat capacity into parts associated with the lattice and the ferroelectric transition will be attempted, the transition entropy will be calculated, and behavior near the transition will be discussed. In Sec. V a comparison of the present results with some theoretical models will be made, together with some concluding remarks concerning the possible interpretation of these results.

II. EXPERIMENTAL DETAILS

The calorimetric measurements were made using apparatus and techniques previously described more fully.^{2,4} Briefly, the measurements used conventional, discontinuous-heating, adiabatic calorimetry, using an appropriate low-temperature thermistor⁵ as a temperature sensor. Under favorable conditions, temperatures could be determined with a precision of approximately $50 \mu^\circ\text{K}$. The thermistors were calibrated against a Pt resistance thermometer, which in turn was calibrated by the National Bureau of Standards according to the International Practical Temperature Scale. Because of possible calibration shifts in the thermistors, the temperature scale has an accuracy far worse than its precision; the over-all accuracy is estimated to be about 0.1°K .

In addition to the conventional measurements, continuous-heating and cooling experiments were conducted. In the continuous-cooling experiments, the adiabatic shield was held at a constant temperature, approximately 2°K below the transition, and the sample was allowed to cool by radiation. Continuous-heating experiments were performed by adding heat electrically to the sample heater, either with the shield at the same temperature as in the cooling experiments or at the same temperature as the sample. A systematic error of about 0.01°K occurred in the temperature scale when the shield was cooler than the sample because of radiational cooling of the thermometer. Thus the most reliable such data were obtained during heating with temperature differences smaller than a few m°K between the sample and the shield. Heating rates of $10^{-4}^\circ\text{K}/\text{sec}$ or less were used. However, good agreement between the continuous-heating experiments and the discontinuous-heating measurements was observed only when the heating rate was considerable less than $50 \mu^\circ\text{K}/\text{sec}$.

Samples were obtained from Isomet Corp. as single-crystal pieces cut from larger boules. The DKDP sample was the same crystal (12.65 g) on which the previous measurements⁴ were performed, while the KDP sample had a mass of 27.4 g. The usual technique involved wrapping the crystal with a small quantity of copper foil (less than 1 g) on which the heater and thermometer were mounted. The foil was then cemented to the

sample with GE 7031 varnish. Such samples will be referred to as "foil-wrapped" samples.

The heat capacity of the addendum for the foil-wrapped samples was measured at the conclusion of the main measurements. In the addendum measurements, the foil was compressed so that as little surface area as possible was exposed. In one series of measurements, carried out between 80 and 140°K , the KDP and DKDP crystals were measured using the same addendum and thermometer calibration, so that, for this one series, a comparison of the heat capacity of the two isomorphs could be made with a minimum of adverse effects caused by systematic errors in the temperature scale and/or addendum heat capacity.

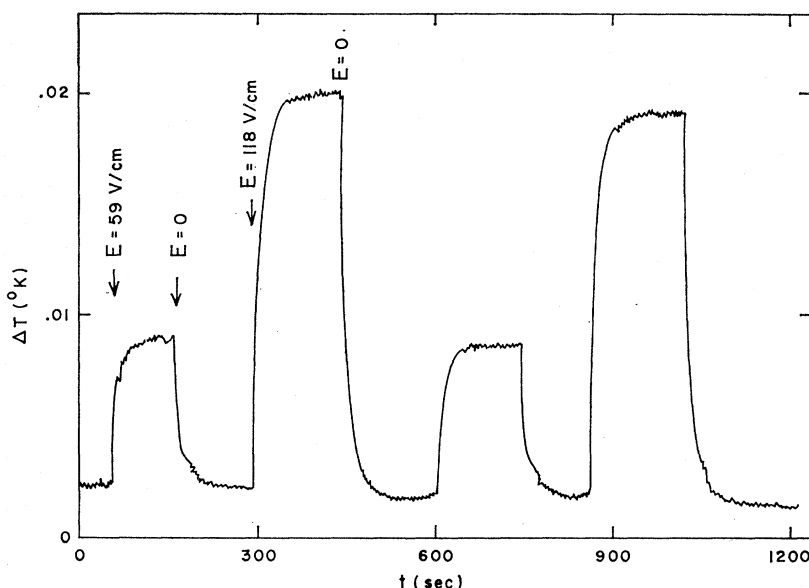
In addition to the series of measurements on DKDP referred to above, a separate series, employing separate addendum measurements and thermometer calibrations, was made between 80 and 180°K . A third series of measurements was made in the range $200\text{--}235^\circ\text{K}$, using the crystal with a minimum of addenda: no foil, only the thermometer, heater, differential thermocouple, mounting strings, and the minimum quantity of GE 7031 varnish needed for mechanical stability. For this series, the heat capacity of the addendum was calculated, using the results of previous measurements of the heat capacity of these materials made in this laboratory. This series of measurements of the heat capacity of DKDP are not reported in detail here, but were incorporated with the other series in Table II. Finally, several measurements, using foil-wrapped samples, were made at about 10°K intervals in the range $240\text{--}280^\circ\text{K}$, using temperature increments of about 0.2°K .

Additional calorimetric measurements were made, and are reported in detail here, on a KDP sample with electrodes attached. The sample was a rectangular plate, $2.30 \times 2.12 \times 0.382 \text{ cm}$, with the short dimension parallel to the ferroelectric axis, which was cut from the original KDP crystal using a wet string saw. Following water polishing, gold electrodes were evaporated on this crystal, which will be referred to as the "plated" sample. The heater and thermometer were mounted on opposite faces, and electrical connections were made to the electrodes. Simultaneous measurements of the dielectric and thermal properties were made using this sample, as were measurements of the heat capacity in applied electric fields and measurements of the electrocaloric effect.

Capacitance measurements of the plated sample were made using a General Radio type 716 capacitance bridge operating at 1 kHz with a peak field of 15 mV/cm . Such small fields give a negligible electrocaloric effect, even in the immediate vicinity of the transition, so that there is no practical distinction to be made between the isothermal and adiabatic susceptibilities. Narrow-band amplification of the output signal from the bridge was employed so that such small measuring fields could be used. During the course of the experiment

⁵ YSI model 44002 (Yellow Springs Instruments) for measurements above 180°K and Keystone Carbon Co. type RL10X04 below 180°K .

FIG. 1. Measurement of the electrocaloric effect made about 0.015°K above the transition in KDP. The second pair of curves duplicates the conditions of the first. This figure, which is a tracing from the recorder output of temperature versus time, demonstrates that the measurements were made under nearly adiabatic conditions.



it was verified that no observable difference in calorimetric measurements resulted if the capacitance bridge was operating, if the sample leads were shorted, or if the sample leads were open-circuited during measurements.

Measurements of the electrocaloric effect—the temperature change accompanying an adiabatic field change—were made by switching the sample between an appropriate battery and a short circuit. One set of measurements, which was taken about 0.015°K above the transition, is shown in Fig. 1. The slight base-line drift is caused by radiational cooling from the sample, due to the inability of the adiabatic shield to follow the rapid temperature variations of the sample. Except for the base-line drift, the measurement in Fig. 1 demonstrates the reversibility of the effect observed.

III. NATURE OF THE FERROELECTRIC TRANSITION IN KDP

A. Calorimetric Measurements in Zero Field

The present calorimetric data agree to within 0.1% with the earlier data of Stephenson and Hooley¹ more than 15°K away from the transition, so that, other than noting this excellent agreement, such data will not be discussed. In addition, the differences between the current results and previous data^{1,2} seem adequately explained by differences in transition temperature⁶ as close as a few hundredths of a degree to the transition.

The present heat-capacity data, obtained from the discontinuous-heating measurements on the foil-wrapped sample in the immediate vicinity of the transition, are presented in Fig. 2. Because of the very

rapid temperature variation, a plot of $\log_{10} C$ as a function of T is shown. Even in this compressed presentation, the temperature dependence of C increases markedly in the neighborhood of the dashed line, which is taken to represent the transition temperature. The points for which the initial and/or final temperatures fall above this temperature are thought to represent measurements on a superheated sample.

If the transition is of first order, as implied by the above interpretation, the most revealing variable

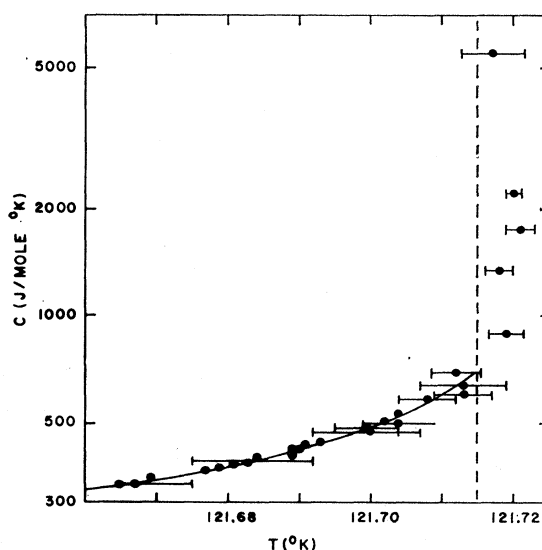


FIG. 2. Heat capacity of the "foil-wrapped" sample of KDP, deduced by discontinuous-heating experiments, shown in the neighborhood of the ferroelectric transition. The horizontal bars give the temperature range, initial to final, over which the point was taken and are typical of all points in vicinity of the points so marked. The dashed vertical line is thought to represent the transition temperature. The solid curve has no significance other than that of fitting the data.

⁶ The transition temperature given in Ref. 2 was in terms of a provisional temperature scale which the current scale replaces. Stephenson and Hooley find the transition on their scale to occur 0.26°K higher than is found in the present work. Whether this difference is real or merely reflects different temperature scales does not seem germane at this point.

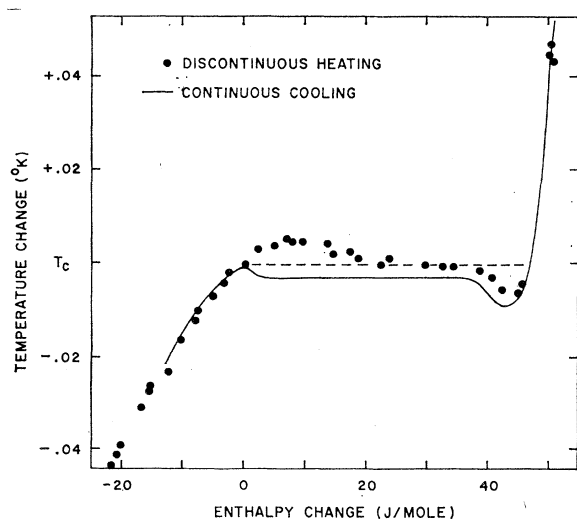


FIG. 3. Enthalpy-temperature relationship deduced for the "foil-wrapped" sample of KDP. The discontinuous-heating data were taken from calorimetric data such as those shown in Fig. 2. The continuous-cooling curve was obtained under conditions discussed in the text. The dashed line shows the assumed thermal equilibrium enthalpy-temperature relationship. The evidence of superheating and supercooling as well as the isothermal absorption of heat mark the transition as one of first order.

against which to plot measured quantities is the enthalpy (which, to within an additive constant, is the heat supplied), since in the two-phase region the portion of the sample which has undergone the phase transition will be linear in enthalpy. In Fig. 3, the heat-capacity data have been recast in the form of an enthalpy-temperature plot. The curve is reproducible, since the points represent the results of many independent passes through the transition. This presentation of the data shows an isothermal absorption of heat and both superheating and supercooling. These features establish the transition as being of first order. Because of the superheating, it is difficult to give an unequivocal value for the latent heat, but on the basis of the assumed transition temperature, indicated by the dashed lines in Figs. 2 and 3, the latent heat is found to be 46.2 ± 0.2 J/mole. The uncertainty indicates the reproducibility over seven independent determinations. A much larger uncertainty is due to the problem of locating the transition,⁷ so that, if this uncertainty is included, the final result for the latent heat is $46.2_{-6.0}^{+4.5}$ J/mole.

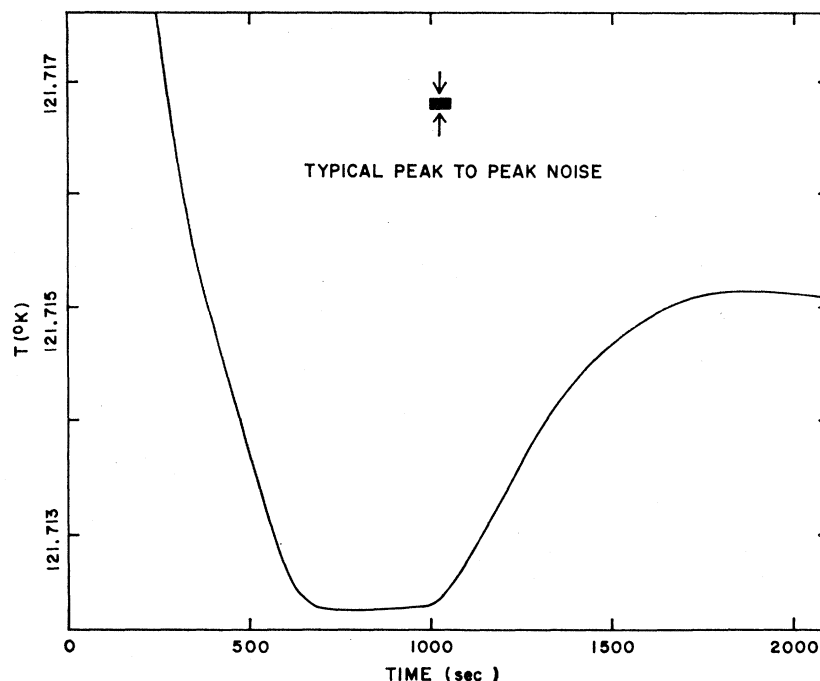
Also shown in Fig. 3 are the results of a continuous-cooling experiment. In this experiment heat was removed from the sample at the rate of 0.79 mJ/sec, producing a cooling rate of less than $60 \mu\text{K/sec}$. The cooling rate was determined by matching the latent heat obtained from the continuous-cooling experiment

with that obtained from the discontinuous-heating data. The cooling rate so obtained was consistent with values obtained by matching the heat capacity determined by the two techniques about 0.2°K above the transition. Two small shifts have been made in the temperature scale in the cooling experiment. The first shift, about $1 \text{ m}^\circ\text{K}$ to higher temperatures, was made to correct for small temperature gradients in the sample which resulted because cooling took place from the surface. Thus, the average sample temperature is actually slightly higher than the surface temperature. This correction was found by a comparison of cooling curves taken at different cooling rates with extrapolation to zero cooling rate. The second correction, about $12 \text{ m}^\circ\text{K}$ to higher temperatures, accounts for the imperfect thermal contact between the sample and thermometer. Because of radiation to the shield, the thermometer was cooler than the sample. This correction was determined by comparing cooling experiments with continuous-heating experiments in which the shield was held at the same temperature as during the cooling experiments. After correcting for temperature gradients in the sample, as discussed above, the cooling and heating experiments gave the same transition temperature to within $0.1 \text{ m}^\circ\text{K}$, but $12 \text{ m}^\circ\text{K}$ lower than in the discontinuous-heating experiments. Considering all of the corrections which have been made to the continuous-cooling data, the agreement with the discontinuous-heating data is perhaps less impressive than might appear at first glance. However, the data show an isothermal absorption of heat and supercooling, which again mark the transition as being of first order.

The enthalpy curves display several other noteworthy features. One feature is the unusual supercooling effect observed at the paraelectric side of the heating transition, i.e., a region of apparent negative heat capacity following the region in which heat is absorbed isothermally. This feature is thought to be associated with the presence of ferroelectric domains. During the heating transition, the domains must be reduced in number and/or size until they vanish. Since electrostatic and other considerations require a reasonably large number of domains, the domains must become quite small near the end of the heating transition. Since small domains are unfavorable in terms of the domain-wall energy, it is hypothesized that at some point it is less costly in terms of the total free energy (including the effects of external fields and domain walls) for the material to make the paraelectric transition suddenly, and to obtain the required heat by supercooling the resulting paraelectric, rather than to make the remainder of the transition at equilibrium. Conversely, there is a slight "superheating" effect on the ferroelectric side of the cooling transition, which seems to be related. This effect is thought to represent a transition by the last vestiges of the paraelectric material, before sufficient heat has been removed to allow the entire transition to occur at equilibrium. It is hypothesized that this "superheating

⁷ In a preliminary report of this work [W. Reese, *Bull. Am. Phys. Soc.* **13**, 504 (1968)], a different value, 50.5 J/mole, was reported. This value was obtained with different assumptions concerning the nature of the phenomena at the transition, and assumed that the lowest temperature reached after the isothermal absorption of heat represented the true transition temperature.

FIG. 4. Shown here is a reconstruction of the thermometer response following a large heat input while the "foil-wrapped" sample was at the temperature of the ferroelectric transition. The heat input caused the outer portion of the sample, to which the thermometer is most closely coupled, to make the transition entirely into the paraelectric state. The subsequent behavior demonstrates supercooling. The final equilibrium temperature is near the dashed line in Fig. 3.



on cooling" occurs when a further reduction in size of the paraelectric regions would cause the surface terms (probably of the same order of magnitude as domain-wall energies) to outweigh the volume terms, which tend to keep the sample partly in the paraelectric state. The heat liberated in the sudden transition of the paraelectric vestiges superheats the ferroelectric. We assume that the effect on heating is larger than the effect on cooling both because the heat capacity of the paraelectric is smaller than that of the ferroelectric and because the domain structure requires larger volumes to be involved in the heating effect. Quantitative deductions about the size of the domain-wall energy could be made from this data, provided that the volumes involved in the processes were known.

An additional supercooling effect is shown in Fig. 4, where the equilibration of the sample following a large (about 80% of the latent heat) heat input is plotted. The plot has been reconstructed from the original thermometer output versus time recording. Following an initial recovery from an overshoot, which results because the thermometer was more closely coupled to the heater than to the sample, the temperature of the thermometer (and probably the outer portion of the sample) stabilizes at a temperature characteristic of the supercooled paraelectric in the enthalpy plot of Fig. 3. The succeeding warming is interpreted as occurring when the outer portion of the sample has lost sufficient heat to the interior so that the supercooled paraelectric is no longer stable. One or more ferroelectric domains are then formed in the outer portion of the sample,

liberating sufficient heat to cause the observed temperature rise. The final equilibrium temperature is approximately on the dashed line of Fig. 3. Although it is attractive to associate the supercooling with the domain structure, this association is not necessary, since an effect such as this only requires that the transition be of first order.

Figure 5 shows a enthalpy-temperature plot obtained in a continuous-heating experiment using the "plated" sample and a heat input of 0.45 mJ/sec. During this experiment the shield was held at the sample temperature, so that no major corrections to the temperature scale were made. The heat input was assumed to be only the measured electrical heat input. A different transition temperature than that found for the foil-wrapped sample was indicated. Since it was later verified by recalibration that a shift of the calibration of the thermistor had occurred, there is insufficient evidence to support the shift as an important effect. If the shift is real, it might well indicate the effects of partial clamping caused by the electrodes or of strains developed in preparing and/or cooling the sample.

Comparison of Fig. 5 to Fig. 3 shows a much smaller isothermal region and no superheating. Thus the transition shown in Fig. 5 has the appearance of being nearly of second order. However, the data are interpreted as indicating the appearance to be illusory, for the data are consistent with a first-order transition, broadened over a temperature interval of about 0.04°K. The broadening may be due to effects either of sample preparation or of the evaporated electrodes (perhaps

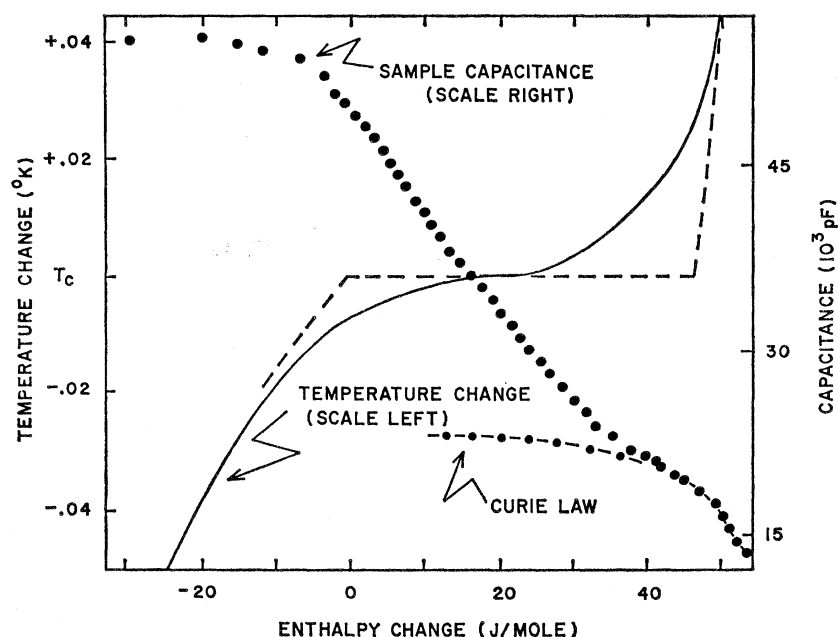


FIG. 5. Sample temperature and capacitance for the KDP plated sample shown as functions of enthalpy. The solid curve shows the temperature-enthalpy behavior as deduced from a continuous-heating curve. The dashed line shows the assumed thermal equilibrium transition deduced from the "foil-wrapped" sample. The Curie law was determined from equilibrium measurements made at temperatures higher than those shown here. It is thought that the region between the maximum capacitance and the Curie-law behavior represents a first-order transition broadened by sample effects.

partial clamping).⁸ This interpretation is confirmed by capacitance measurements, also shown in Fig. 5, which were made during the heating measurements. The capacitance measurements will be discussed Sec. III B. The assumed equilibrium transition from Fig. 3 is indicated in Fig. 5 by the dashed line. This assumed transition encompasses the transition indicated by the capacitance measurements, thus showing that the same value of latent heat as obtained before is consistent with the data shown in Fig. 5.

A final remark, which indicates the first-order nature of the transition and the coexistence of two phases, can be made concerning the time required to obtain equilibrium following an input of heat. Figure 4 is typical of both the foil-wrapped sample and the plated sample, in that thermal equilibrium following an input of heat took approximately 1 h when the sample was in what has here been interpreted as a two-phase condition. When the sample was definitely in a single-phase condition—for example, by being several tenths of a degree from the transition—equilibration following the input of heat typically required 5 min. Thus, in the phase transition region, the thermal equilibrium time was not limited by the diffusion of heat, unless a very low thermal conductivity pertains in a very narrow temperature region, but rather by a longer time, characteristic of the establishment and/or rearrange-

ment of interphase boundaries. Such long equilibration times in the neighborhood of the transition were first noted by Stevenson and Hooley.¹ As a final remark on this point, some unusual equilibration curves were observed at the paraelectric end of a pass through the phase transition. Typically, the equilibration would begin as though with a long time constant and then suddenly achieve equilibrium, as though the phase transition process had come to an end and rapid equilibration, limited by the diffusion of heat, ensued.

B. Dielectric Measurements

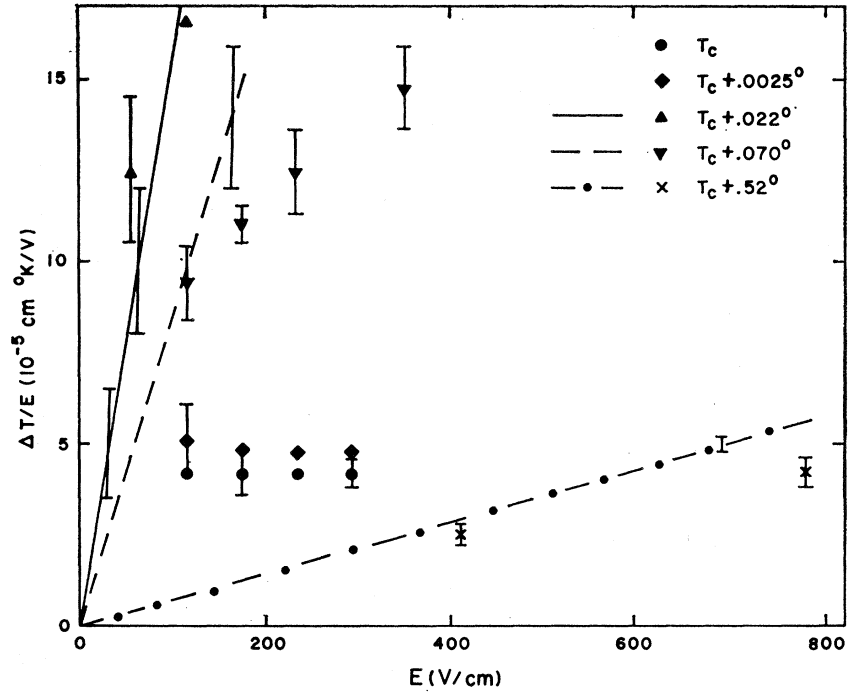
The results of the dielectric measurements can be summarized by stating that the same general results as reported by many others^{3,9} were observed, namely, the susceptibility obeyed the Curie-Weiss law above the transition and decreased very slowly with temperature below the transition. The Curie-Weiss temperature needed to fit the present results was approximately 0.11°K less than the transition temperature, in remarkably good agreement with Craig,³ who found a Curie-Weiss temperature 0.115°K less than the transition temperature observed on heating. (Craig observed a hysteresis of about 0.050°K which was not observed in the present work.)

The most interesting dielectric results are those shown as a function of enthalpy in Fig. 5. Superficially, the maximum in the dielectric constant occurs about 0.04°K below the point of maximum heat capacity. There is then a region in which the dielectric constant

⁸ Subsidiary continuous-heating experiments on the plated sample, before and after the electrodes were mechanically removed, showed superheating only after the electrodes were removed. This strongly indicates that the major cause of the apparent change in the form of the enthalpy-temperature plot was the presence of the electrodes rather than the cutting of the sample. The most likely effect of the electrodes was in partially clamping the sample, as evidenced by small surface cracks which were discovered in the sample when the electrodes were removed.

⁹ The earlier work is summarized in such references as W. Kanzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 1.

FIG. 6. Summary of some of the electrocaloric effect data showing the ratio of temperature change to field change as a function of electric field. The temperatures refer to the temperature of the sample in zero field. T_c is the temperature of the heat-capacity maximum in zero field. The lines show the behavior expected for the paraelectric phase if nonlinear effects are neglected as calculated by Eq. (3). The error bars given for some of the experimental points are typical values for all of the points given. The errors associated with the calculated curves show the uncertainty in the Curie-Weiss temperature.



decreases almost linearly with increasing enthalpy, followed by a Curie-Weiss law dependence on temperature. This last feature is obscured in an enthalpy plot. These observations have a rather natural explanation if it is assumed, as in the previous section, that the region between the maximum in the dielectric constant and the Curie-Weiss law represents a sample in which two phases, ferroelectric and paraelectric, coexist. In terms of this model the ferroelectric phase has a dielectric constant approximately twice that of the paraelectric phase at the transition temperature. The dependence of the sample capacitance, and hence apparent dielectric constant, on enthalpy in the transition region then shows the low-dielectric-constant paraelectric phase growing at the expense of the high-dielectric-constant ferroelectric phase. Since the volume in the paraelectric phase should be linearly related to the enthalpy, the most simple, but not the only, interpretation of the linear enthalpy dependence of the capacitance through the bulk of the transition region is that, in this region, the paraelectric and ferroelectric phases extend in patches through the entire thickness of the sample. The total capacitance is then calculated as the parallel combination of two capacitors whose area is a linear function of the enthalpy. The behavior at either side of the linear region represents a more complicated two-phase pattern, perhaps reflecting the conditions at the edges of the sample.

C. Electrocaloric Measurements

In addition to the calorimetric and dielectric measurements, studies of the electrocaloric effect were made on

the plated sample. These measurements support the conclusion reached in the previous section, that the sample was still at least partly ferroelectric at temperatures above those at which the dielectric constant and the heat capacity were maximum. This supports the hypothesis of a broadened transition in the plated sample.

Thermodynamics shows that

$$\left(\frac{\partial T}{\partial E}\right)_S = -\frac{T}{C_E} \left(\frac{\partial P}{\partial T}\right)_E, \quad (1)$$

where C_E is the heat capacity at constant field and P is the spontaneous polarization. In the ferroelectric phase $(\partial P/\partial T)_E$ is nonzero, even in zero field, while in the paraelectric phase it is zero in zero field. This leads to a useful experimental test for spontaneous polarization in the sample. In the ferroelectric phase, if the field changes are sufficiently small, one can approximate all of the terms in Eq. (1) by constants to find that the temperature change associated with the adiabatic application of a field is given by

$$\Delta T = -\frac{T}{C_0} \left(\frac{\partial P}{\partial T}\right)_0 \Delta E, \quad (2)$$

where the subscript refers to zero field. Thus the temperature change is linear in the applied field, for small enough fields, when spontaneous polarization is present. For purely paraelectric material, if the fields are sufficiently small so that nonlinear effects can be neglected, the polarization is given by $KE/(T-T_0)$, where K is

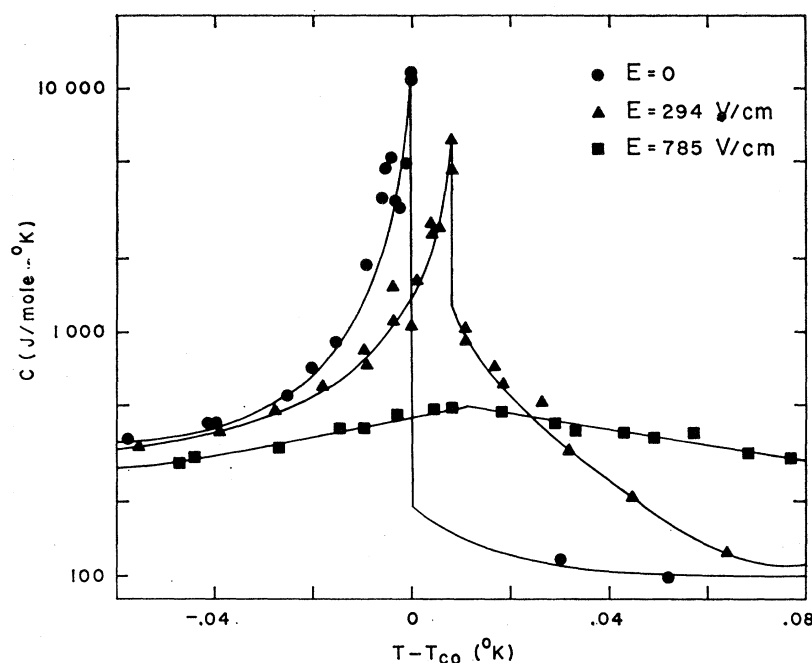


FIG. 7. Heat capacity of the KDP "plated" sample in various applied electric fields. The continuous curves are primarily intended to organize the data presented rather than to depict the true form of the transition. As discussed in the text, the transition in zero field is thought to be a broadened first-order transition, so that the appearance of a second-order transition given by the solid curve is largely illusory. There was some evidence of a small latent heat associated with the transition with $E=294$ V/cm, but the available evidence concerning this point is highly equivocal. No evidence of a latent heat was seen for the transition with $E=785$ V/cm. T_{c0} is the temperature of the heat-capacity maximum in zero field.

the Curie constant and T_0 is the Curie-Weiss temperature. Under these assumptions, one expects a quadratic electrocaloric effect

$$\Delta T = \frac{T}{2C_0} \frac{K}{(T - T_0)^2} (\Delta E)^2. \quad (3)$$

The results of the electrocaloric measurements are summarized by Fig. 6, in which the results of measurements at five temperatures are shown. T_c is taken to be the temperature of the heat-capacity maximum. The temperature of a series of measurements is taken to be the temperature of the sample in zero field. The electrocaloric effect is linear in field for a small range of temperatures below the temperature of the heat-capacity maximum. Those measurements which indicate an electrocaloric effect approximately quadratic in field are compared with calculations using Eq. (3), where the Curie-Weiss temperature is taken to be $T_c - 0.11^\circ\text{K}$, as found from the dielectric measurements, and the Curie constant was taken from Craig's results.

The latter data show departures from the quadratic field dependence predicted by Eq. (3), which indicates the effects of nonlinearities. Although it is possible to extend the treatment of the electrocaloric effect to include nonlinear effects, the estimates of the nonlinear terms in the susceptibility which could be made by an analysis of the electrocaloric measurements would not be useful, since much more precise measurements can be obtained directly by determining the field dependence of the dielectric constant. The present results do point out that nonlinear effects occur at very low values of applied electric field near T_c . Thus, one must use

care in interpreting the results of Baumgartner¹⁰ on the field dependence of the dielectric constant and related measurements, since the fields employed in his work were considerably in excess of 500 V/cm, which would cause considerable nonlinearities near T_c .

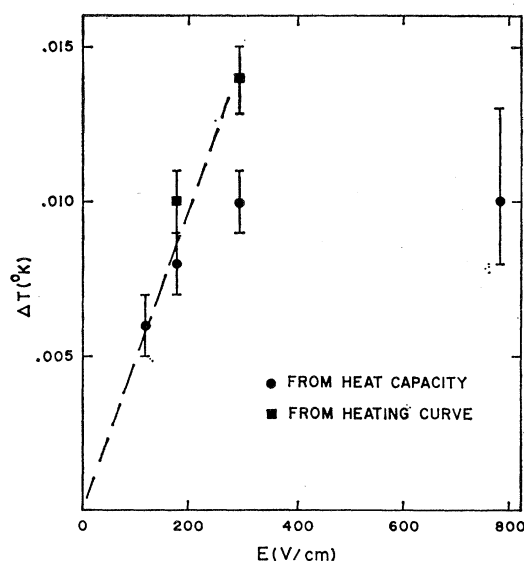


FIG. 8. Shift in transition temperature as measured by the position of the heat-capacity maximum shown as a function of applied field. The dashed line is the assumed linear shift at low fields. Data taken from continuous-heating experiments tend to give too large a value for the shift, so that the points taken from the heat-capacity data should be given most weight in assessing the true shape of the curve. Particularly noteworthy is the fact that little, if any, additional shift is caused by fields in excess of 300 V/cm.

¹⁰ H. Baumgartner, *Helv. Phys. Acta* **23**, 651 (1950).

TABLE I. Thermodynamic parameters characterizing the ferroelectric phase transition in KDP and DKDP in zero field and pressure. L is the latent heat, dT_c/dp and dT_c/dE are the shifts of the transition temperature with pressure and electric field, and ΔP and ΔV are the discontinuous jumps in spontaneous polarization and volume.

	T_c (°K)	L (J/mole)	dT_c/dp (°K/kbar)	Eq. (5)	ΔV (cm ³ /mole) Measured	dT_c/dE (10 ⁻⁴ °K cm/V)	ΔP (μC/cm ²) Eq. (4)
KDP	121.71	46.2	-4.52±0.06 ^a -5.56±0.3 ^c	-0.017±0.001 0.021±0.001	0.022±0.02 ^b 0.03 ±0.02 ^d	0.47±0.05	0.31±0.03
DKDP	219.62 ^e	440 ^e	-2.63±0.05 ^a 3.9 ±0.2 ^g	-0.053±0.001 -0.079±0.005	0.057±0.006 ^e	1.9 ±0.3 ^f	6.5 ±1.0

^a Reference 15.

^b Reference 20.

^c Reference 16.

^d Reference 19.

^e Reference 4.

^f Reference 18.

^g Reference 17.

D. Measurements in Electric Fields

In addition to the calorimetric measurements in zero field, a number of calorimetric measurements were made in applied electric fields. The results of some of these measurements are presented in Fig. 7, where the results of measurements at three different fields are shown. The effect of the field is to shift the transition to higher temperatures, to lower the heat capacity at temperatures below the transition, and to increase it at temperatures above the transition. At a field of 785 V/cm, the pronounced λ -like heat-capacity curve has become a smooth curve which is almost symmetric about the temperature of the heat-capacity maximum. More dramatic alterations of the shape of the heat-capacity curve by fields have been reported for triglycine sulphate,¹¹ in which the transition in zero field is apparently of second order.

Figure 8 shows the shift of the temperature of the heat-capacity peak as a function of field derived from both discontinuous-heating calorimetric studies and continuous-heating experiments. At low fields, the shift of the transition seems linear in field, with $dT_c/dE = (4.7 \pm 0.5) \times 10^{-5}$ °K cm/V. Clapeyron's equation, in the form

$$\frac{dT_c}{dE} = \frac{\Delta P V_m}{\Delta S}, \quad (4)$$

where V_m is the molar volume and ΔP is the discontinuous change in spontaneous polarization at the transition, gives $\Delta P = (3.1 \pm 0.3) \times 10^{-7}$ C/cm², when the results of the present work are used.

For fields much in excess of about 300 V/cm the application of electric fields causes very little, if any, additional shift in the temperature of the transition. Additionally, there is little, if any, evidence from the calorimetric studies of any latent heat for such fields. This indicates that the transition (if indeed it is appropriate to define a transition under such circumstances) loses its first-order character above 300 V/cm.

E. Comparison with Previous Results

If, as has been argued above, the ferroelectric transition in zero field in KDP is of first order, this result

should be reconciled with the previous results. Each of the previous experiments employed sufficiently small heat increments so that an isothermal absorption of heat would not have been overlooked. There seem two possible explanations, both based on the fact that previous measurements have been made on polycrystalline samples with ill-defined electrical boundary conditions. The simplest explanation is that different crystals, even when grown from the same batch, have different transition temperatures, which obscures the nature of the transition in a polycrystalline sample. As an example, differing samples of the antiferromagnet MnF₂ were found to have transition temperatures as much as 0.1°K apart,¹² and even larger shifts of transition temperature with impurity content have recently been investigated in the ferromagnet Gd.¹³ A second possibility is that, because of the pyroelectric effect, some of the crystals in a container of small crystals find themselves under electric fields during the course of the calorimetric experiment. This would shift and broaden the transition. This latter interpretation of the heat capacity of polycrystalline ferroelectric samples has previously been discussed by Strukov.¹⁴ A third, but much less likely, explanation could be that large and small crystal samples exhibit differing behaviors. Since cooling curve measurements using large fragments and pulverized crystals show that the transition temperature is independent of crystal size with a precision of 0.1°K,¹ and since the samples used in previous experiments had a volume of several mm³ while it has been observed that isolated crystals 10⁻¹⁰ as large showed "normal ferroelectric behavior,"¹⁵ this suggestion seems unlikely to be correct.

The previous² observation of a difference between the temperature of the calorimetric and dielectric anomalies may be related to the influence of electrical boundary conditions imposed by differing surface treatments of crystals with and without electrical contacts or to partial clamping effects of electrodes. In any case, in

¹² D. T. Teany, Phys. Rev. Letters **14**, 898 (1965).

¹³ F. J. Cadieu and D. H. Douglas, Jr., Phys. Rev. Letters **21**, 680 (1968).

¹⁴ B. A. Strukov, in *Proceedings of the International Meeting on Ferroelectricity* (Czechoslovakia Academy of Sciences, Prague, 1966), Vol. 1, p. 191.

¹⁵ C. Jaccard, W. Kanzig, and M. Peter, Helv. Phys. Acta **26**, 521 (1953).

¹¹ B. A. Strukov, S. A. Turaskin, T. L. Skomorokhova, and K. A. Minaeva, Izv. Akad. Nauk SSSR, Ser. Fiz. **29**, 982 (1965).

TABLE II. Heat capacity of DKDP, except in the immediate vicinity of the ferroelectric transition. Data in the vicinity of the transition can be found in Table I of Ref. 4, but those data must be corrected as discussed in the text by adding $2.40 + 0.0306T$ J/mole °K to obtain agreement with the present data.

T (°K)	C (J/mole °K)	T (°K)	C (J/mole °K)
80	46.03	180	89.35
90	51.25	190	93.16
100	55.89	200	98.10
110	60.20	Region of ferroelectric transition	
120	64.40		
130	68.68		
140	72.99		
150	77.25		
160	81.11		
170	85.19		
		230	106.8
		240	108.6
		250	111.0
		260	113.4
		270	115.7
		280	118.2

the present work the same transition temperature is determined calorimetrically and dielectrically when the measurements are made simultaneously on the same crystal.

F. Further Thermodynamic Relationships

The determinations of the latent heat in zero field for KDP and DKDP can be combined with recent determinations of the shift of the critical temperature with pressure¹⁵⁻¹⁸ in Clapeyron's equation to predict the discontinuous change of volume at the ferroelectric transition,

$$\Delta V = \Delta S \left(\frac{dT_c}{dp} \right)_E. \quad (5)$$

These results, together with the results of using Eq. (4) to relate the shift of critical temperature with applied field¹⁹ to the polarization jump, are given in Table I.

While the reported values of the pressure shift of the transition temperature do not agree within the stated errors, the predicted volume changes are reasonably consistent with the best estimates which can be made from available x-ray data.^{20,21} In preparing Table I, a reanalysis of Cook's data has been made. The volume changes originally reported refer to the total change in excess of that expected by normal thermal expansion over an interval of about 10°K, rather than the discontinuous volume change at T_c , which is the value obtained from Clapeyron's equation. The uncertainties in the x-ray data are rather large because of the large uncertainty in extrapolating the lattice constants to T_c , which in turn is due to the very rapid temperature dependence of the lattice constant expected near T_c .

The value calculated for the spontaneous polarization jump for DKDP may be too large, since the crystal on

which Hill and Ichiki¹⁹ made their measurements had a lower transition temperature than the one on which the present calorimetric measurements were made; it therefore presumably had a lower deuterium content and perhaps a smaller discontinuous entropy change as well. If both of the values employed in the calculation of the polarization jump are assumed to be correct, a problem arises, since the calculated value of the jump at the transition may be significantly larger than the most recent experimental values for the spontaneous polarization of 0°K.²² There are, in the opinion of the present author, no really reliable measurements of the polarization in the immediate neighborhood of T_c with which the values calculated using Eq. (4) can be compared.

IV. HEAT CAPACITY OF DKDP AND COMPARISON WITH KDP

A. Heat Capacity of DKDP

In addition to the studies of KDP in the vicinity of the ferroelectric transition, an extensive study of the heat capacity of DKDP in the temperature range 80–280°K was carried out. Five independent experiments involving separate thermometer calibrations and addenda heat-capacity determinations were conducted over various portions of this temperature range. One of these experiments, covering the temperature range 185–235°K, which encompasses the ferroelectric transition, has been previously reported in some detail.⁴

At the conclusion of these experiments, it was discovered that the previously reported results disagreed in the region of overlap with the lower-temperature data and with a second experiment conducted between 205 and 240°K using the crystal with minimum addenda. It was concluded that the addendum heat-capacity determinations employed in the analysis of the previous data were seriously in error because of an incorrect procedure used to account for radiation heat loss during equilibration. To check this conclusion, the addenda from the previous experiment were compressed so as to present as small a radiating surface area as possible, and were re-measured. The new addendum measurements, when applied to the previous data, gave results which agreed with all other sets of measurements. The most serious result of this error is that all the entries in Table I of Ref. 4 should be increased by $2.40 + (0.0306^\circ\text{K}^{-1})T$ J/mole°K. This systematic error had little effect on the analysis presented since a corresponding incorrect estimate of the background heat capacity was also made. After correction of this error in the one set of data, all data sets agreed in regions of overlap to better than 1%; in most cases the agreement was of the order of 0.3%. The data are summarized in Table II.

B. Comparison of KDP and DKDP

If one is to obtain the maximum useful information concerning a phase transition from calorimetric mea-

²² J. L. Bjorkstam and R. E. Oettel (private communication).

¹⁶ H. Umabayashi, B. C. Frazer, G. Shirane, and W. B. Daniels Solid State Commun. **5**, 591 (1967).

¹⁷ E. Higenbarth and S. Ullwer, Cryogenics **7**, 306 (1967).

¹⁸ G. A. Samara, Phys. Letters **25A**, 664 (1967).

¹⁹ R. M. Hill and S. K. Ichiki, Phys. Rev. **132**, 1603 (1963).

²⁰ M. DeQuervain, Helv. Phys. Acta **17**, 509 (1944).

²¹ W. R. Cook, J. Appl. Phys. **38**, 1637 (1967).

surements, one must separate the heat capacity into a background part, here called C_G or lattice heat capacity, and an excess part, which is taken to be connected with the phase transition. A variety of techniques can be adopted to effect the required separation, ranging from a simple guess made by drawing a "reasonable" smooth curve consistent with the data to more elaborate guesses based on fitting the heat capacity away from the transition to functions with theoretical significance, such as one or more Debye functions. In the current instance, any separation of the second type is fraught with dangers, since the transitions occur at elevated temperatures where the lattice-heat-capacity contribution is expected to be large, a fact complicated by the complicated unit cell which will lead to a rich spectrum of possible lattice vibrations. In order to circumvent at least some of these pitfalls, a technique previously employed in the analysis of the heat capacity of DKDP⁴ was adopted, namely, estimating C_G from a comparison of the heat capacities of the normal and deuterated materials. This technique is based on the hope that the lattice heat capacity of the two materials is not too different, even when one is in the paraelectric, tetragonal phase and the other is in the ferroelectric, orthorhombic phase. This seems reasonable since the lattice distortion between phases is quite small. A secondary assumption is that, in the vicinity of a transition in one salt, the heat capacity of the other is entirely, or almost entirely, background heat capacity. This seems reasonable because the transitions are widely spaced in temperature. Regardless of the validity of these assumptions, such a procedure is well defined operationally.

The results of the comparison, concentrating on the regions not too close to the transitions, are presented in Fig. 9. The present measurements of both KDP and DKDP were used below 140°K. The results of the experiment in which heat-capacity measurements were carried out on both isomorphs with the same addendum and temperature scale were weighted most heavily, since the possible effects of systematic errors are then minimized so that the accuracy of the comparison is of the order of the combined precision of the measurements, about 0.25%. At higher temperatures the present DKDP measurements are compared with the KDP measurements of Stevenson and Hooley.¹ Because of the good agreement between the Stevenson-Hooley results and those of the present work, which was cited at the beginning of Sec. III, it is felt that the accuracy of the comparison is better than the combined accuracies of the two measurements. An over-all estimate of accuracy of the comparison shown in Fig. 9 is perhaps $\pm 0.1R$. The heat capacity of DKDP is found to be larger than that of KDP above about 130°K. This seems a remarkable conclusion, with important implications concerning the theoretical analysis of the underlying mechanisms of the phase transition in KDP-type ferroelectrics.

One expects the vibrational frequencies in DKDP to be smaller than in KDP because of the larger mass of

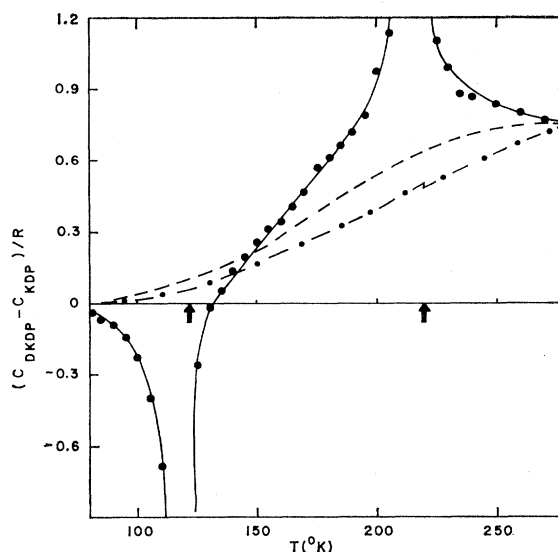


Fig. 9. Difference in heat capacity of KDP and DKDP as obtained from the present results and those of Stephenson and Hooley. The arrows mark the location of the ferroelectric transitions. The dash-dot line gives the result of the simple calculation of the residual difference based on the infrared spectrum outlined in the text. The dashed curve gives the estimate of the residual difference which was used for further analysis. Perhaps the most significant feature of this figure is the scant evidence for a contribution of about $0.5R$ to the heat capacity above T_c due to the residual disordering of protons within the possible H-bond positions.

the deuteron as compared to that of the proton. Thus it is expected that the heat capacity of KDP will be smaller than the heat capacity of DKDP. An estimate of this contribution is shown as the dash-dot line in Fig. 9. This estimate was based on the observed infrared absorption spectrum of the two isomorphs.²²⁻²⁵ The data of Imry *et al.* have been given preference, because these data give absorption spectra for both isomorphs in both phases. It was assumed that the heat capacity associated with optical modes could be calculated using Einstein functions with temperature-independent frequencies. The largest part of the difference in heat capacity in such a calculation comes from the $\gamma(\text{OH})$ and $\delta(\text{OH})$ modes, but the modes associated with PO_4 vibrations also give non-negligible contributions. Account of acoustic modes was taken by employing Debye functions with Debye temperatures scaled by the square root of the unit-cell mass. This last contribution is almost negligible in the temperature range considered, never amounting to as much as $0.01R$.

Although the above calculation has the virtue of simplicity, it does not work particularly well. For example, at 280°K the above calculation underestimates the total heat capacity of both isomorphs by about

²² R. Blinc and D. Hadzi, *Mol. Phys.* **1**, 391 (1958).

²⁴ A. S. Barker and M. Tinkham, *J. Chem. Phys.* **38**, 2257 (1963).

²⁵ Y. Imry, I. Pelah, and E. Wiener, *J. Chem. Phys.* **43**, 2332 (1965).

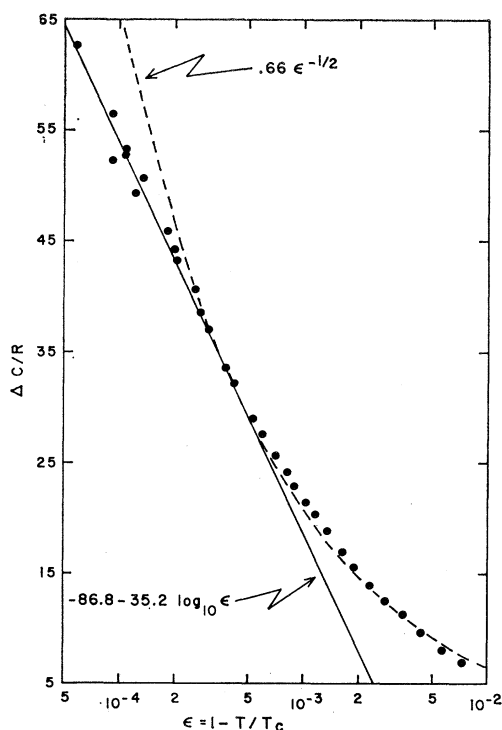


FIG. 10. Behavior of the heat capacity of the "foil-wrapped" sample just below the temperature of the ferroelectric transition. ΔC is the difference between the measured heat capacity and C_G . The two curves are empirical fits to the data.

10–12%. This indicates that the spectrum of lattice vibrations is not nearly so simple as has been assumed. Such assumptions as temperature-independent frequencies for the optical modes are not strictly correct either. The hope on which the calculation is based is that, however the true spectrum of lattice vibrations differs from the simple model, the variation is roughly the same for both isomorphs. Fortunately, the majority of the region of interest is off the scale of Fig. 9, showing that the uncertainties discussed above are not as important as the discussion may make them seem.

The results of the calculation outlined above seems unsatisfactory because, when the calculated curve is taken as the residual difference between the lattice heat capacities, there is little symmetry in $C - C_G$ between the two isomorphs, particularly above the transition temperature. The dashed curve in Fig. 9, which represents a compromise between the simple calculation outlined above and a desire for a degree of similarity in the transitions of the two isomorphs, has been adopted for further analysis. Uncertainty in the difference between C_G for the two substances is of the order of a few tenths of R unless the assumptions on which the estimate was made are invalid.

The analysis shows that $C' - C_G$ is small for KDP at any temperature above 140°K, seemingly with any reasonable assumption as to the residual difference in lattice heat capacity. This result was anticipated in a

previous, much simpler, estimate of the lattice heat capacity of KDP.² Here the conclusion seems almost inescapable, unless one assumes that $C - C_G$ for DKDP is non-negligible at much lower temperatures than might be expected from the temperature dependence of the spontaneous polarization, or that there are large differences in C_G between the tetragonal and orthorhombic phases. This conclusion is surprising, since the most widely accepted theories of the ferroelectric transition in KDP are elaborations of an idea presented long ago by Slater,²⁶ that the transition could be understood in terms of the ordering of protons in the available H-bond positions. Any such theory predicts a sizeable contribution to the heat capacity due to disordering process (about $0.5R$) for a sizeable temperature region (about 100K°) above the ferroelectric transition. Since the estimates of lattice heat capacity made here are not expected to be wrong by such a substantial amount, little evidence for the existence of such a heat-capacity contribution is found.

C. Transition Entropy and Behavior near T_c

Using the measured heat capacity of DKDP and KDP and the estimate of the residual difference between C_G for the two isomorphs given by the dashed line in Fig. 9, an estimate of C_G for both materials is available. Using this estimate of C_G , the entropy change associated with the ferroelectric transition to T_c is $(0.457 \pm 0.034)R$ for DKDP and $(0.400 \pm 0.036)R$ for KDP. The quoted uncertainties take into account *both* the uncertainties in the experimental data and the much larger uncertainties in the lattice-heat-capacity estimate. These values differ somewhat from previous determinations of the transition entropy primarily because a different estimate of the lattice heat capacity was made. No attempt was made to calculate the entropy difference above T_c (which is presumably associated with the destruction of short-range order), since the heat-capacity excess is small, and the value obtained in such a calculation depends critically on the estimate of C_G .

Using the present estimate of C_G , the behavior of the heat capacity in the neighborhood of the phase transition can be examined. Such an examination for KDP, using data from the "foil-wrapped" sample, is presented in Fig. 10. Only the results below T_c are examined, since any uncertainty in C_G is much more important above T_c than below and can seriously prejudice the analysis above T_c . In the region $10^{-2} > \epsilon > 3 \times 10^{-4}$, the heat capacity seems proportional to $1/\epsilon^{1/2}$, which is the well-known Ornstein-Zernike result. However, in the region inside about $\epsilon = 2 \times 10^{-4}$, there seems a decided preference for a logarithmic fit. In Fig. 10 any points which may have been affected by superheating have been excluded by casting out any points for which the initial and/or final temperature fell above the dashed line in Fig. 2. Very similar behavior was observed for

²⁶ J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

DKDP, namely, a $1/\sqrt{\epsilon}$ dependence starting at about $\epsilon=10^{-2}$ which went over to a logarithmic dependence closer to the transition. The behavior in KDP is much more pronounced than in DKDP, as one might expect in terms of the usual interpretation of "critical-point" phenomena, since the transition in KDP is much more nearly of second order than in DKDP.

Because the transition is of first order and may be somewhat broadened, it is difficult to decide if one or the other of these temperature dependencies represents the "true" behavior in the vicinity of the phase transition or if the apparent rapid transition from one form to the other is a real effect rather than an artifact of the experiment. However, the author does view the results as offering quite interesting suggestions concerning the behavior of the heat capacity near the transition.

V. COMPARISON WITH THEORETICAL MODELS

The simplest model with which one can compare our results is the phenomenological model, widely identified with Devonshire²⁷ in the field of ferroelectricity, which in the current instance is equivalent to the Landau²⁸ expansion of the free energy. In this model one expands the free energy per unit volume as

$$F = F_0 + (1/2K)(T - T_0)P^2 + \frac{1}{4}\gamma P^4 + \frac{1}{6}\delta P^6, \quad (6)$$

where the coefficients are assumed, in the absence of contrary evidence, to be temperature-independent and are chosen to fit experiment. In the above, F_0 is the free energy with zero polarization, K is the Curie constant, T_0 is the Curie-Weiss temperature, and P is the polarization. The thermodynamic results of this assumed equation of state have been thoroughly explored,²⁹ so that we will use the results without derivation.

The difference between T_c and T_0 and the latent heat could be used together with the Curie constant to evaluate the parameters in Eq. (6). From this the expected behavior in the electrocaloric measurements and heat-capacity measurements in fields, etc., could be computed. Such a procedure has little merit, since the theory does not seem to work particularly well in the immediate neighborhood of the ferroelectric transition where the bulk of the current work is concentrated. However, before making an examination of this point, it may be well to point out a success of the theory. The transition entropy is predicted to be

$$\Delta S = (1/2K)P_0^2, \quad (7)$$

where P_0 is the spontaneous polarization at 0°K. Using the most recent values for P_0 ²² and K ,³⁰ the model

²⁷ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949); **42**, 1065 (1951); *Advan. Phys.* **3**, 851 (1954).

²⁸ L. D. Landau, *Zh. Eksperim. i Teor. Fiz.* **7**, 1232 (1937).
²⁹ Perhaps the most detailed exposition is that of E. Fatuzzo and W. J. Merz, *Ferroelectricity* (North-Holland Publishing Co., Amsterdam, 1967), Chap. 3.

³⁰ R. J. Mayer and J. L. Bjorkstam, *J. Phys. Chem. Solids* **23**, 619 (1962).

predicts $\Delta S/R = 0.452$ for DKDP and 0.352 for KDP. Since there is about a 10–20% uncertainty in the calculated value, reflecting the uncertainty in P_0 , rather good agreement between this calculation and the present experimental results is found. This does not contradict the claim concerning the failure of the theory to describe KDP near T_c , since the bulk of the transition entropy comes from more than 1°K below T_c .

Ginzburg³¹ pointed out some time ago that one does not expect the Landau theory to work well near a phase transition because of the effects of fluctuations, which become particularly serious if the transition is of second order or is nearly of second order (as in the case of KDP). Since it is not surprising that the theory would encounter difficulties near T_c , only the most obvious failure will be noted. Based on the present latent heat measurement one would predict that the spontaneous polarization jump would be about 34% of P_0 , which is to be contrasted with a jump of about 6% of P_0 deduced from the present measurements through the Clayperon equation.

Having pointed out that the Landau theory is inadequate to describe KDP in the immediate vicinity of T_c , the question of interest is how near one must get to T_c before the inadequacy becomes apparent. Since there are no sufficiently precise measurements of the spontaneous polarization available to test the prediction

$$\Delta C = (T/2K)(d/dT)(P^2), \quad (8)$$

only a few general comments on the question can be made. Taken strictly, the Landau theory does not predict the $1/\sqrt{\epsilon}$ dependence of ΔC which is observed for $\epsilon < 10^{-2}$. From this point of view one might suspect that the $\epsilon = 10^{-2}$ marks the region of validity of the free-energy expansion. If true, this may be considered rather surprising, since, in his consideration of the region of validity of the Landau theory to ferroelectrics, Ginzburg estimated the region of validity to be outside $\epsilon \approx 10^{-4}$, because of the long range of the interactions involved. If $\epsilon = 10^{-2}$ marks the range of validity of the Landau theory, when applied to KDP, this is an indication that the relevant interactions have a short range in KDP, as envisaged by theories of the Slater type. On the other hand, it seems possible to argue that the Ornstein-Zernike $1/\sqrt{\epsilon}$ dependence of ΔC represents the same type of account of short-range correlations (in the mean) as is implied by the Curie-Weiss law, and hence that, while not predicted by the Landau theory, this dependence of ΔC is compatible with microscopic models which lead to the same relationship between P and E . In this way it seems possible to argue that the Landau theory should be essentially valid, at least as far as the relationship between P and E is concerned, until the Ornstein-Zernike dependence of the heat capacity is seriously violated, which is around 2×10^{-4} for KDP. (See note added in proof.)

³¹ V. L. Ginzburg, *Fiz. Tverd. Tela* **2**, 2031 (1960) [English transl.: *Soviet Phys.—Solid State* **2**, 1824 (1960)].

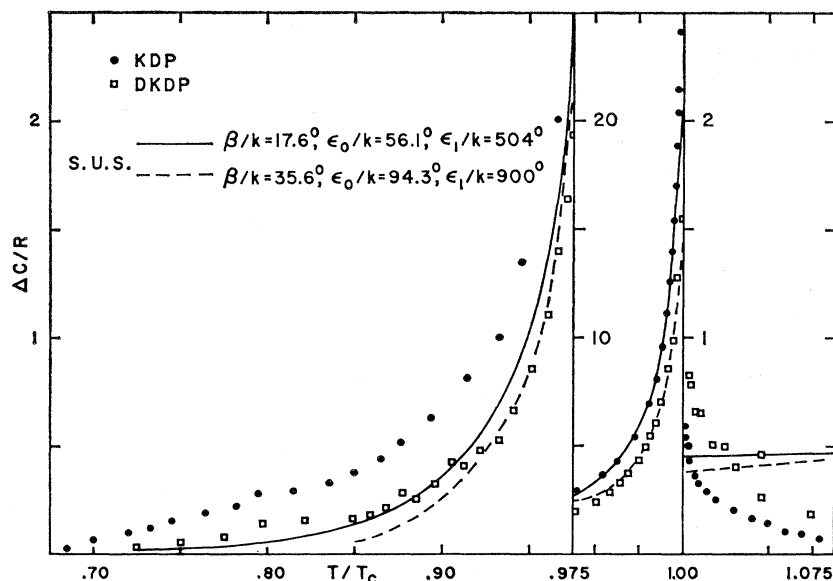


FIG. 11. Heat-capacity excess $C - C_0$ for KDP and DKDP as deduced from our measurements and the lattice estimate as shown in Fig. 9. Note the changed vertical and horizontal scales in the region $0.975 < T/T_c < 1.0$. The curves are calculated using the SUS theory with parameters chosen to fit the data near $T/T_c = 0.96$.

A completely different approach from that embodied in Eq. (6) consists of detailed calculations based on microscopic models. For KDP the best developed among such models are elaborations of the original Slater model which consider that the ordering of protons in the possible H-bond positions plays an essential role in the phase transition.³²⁻³⁶ However, as emphasized by Tokunaga and Matsubara,³⁶ it is essential to include a coupling of the proton ordering to the motions of the K^+ and PO_4^- ions in order to explain the spontaneous polarization. Because of its greater simplicity, the model of Silsbee, Uehling, and Schmidt³⁴ (SUS) will be emphasized. This model will not be expected to work as well for KDP as for DKDP because of the neglect of tunneling.

In the SUS model, one introduces three parameters: ϵ_0 and ϵ_1 , which give the energy of various proton configurations, and β , which is a mean-field term. The parameter ϵ_1 has been measured for DKDP by the analysis of the temperature dependence of the NMR relaxation time. The transition temperature is taken as an input parameter, reducing the number of free parameters to one in the case of DKDP and two for KDP. One expects the energy parameters ϵ_0 and ϵ_1 to be related to the proton off-center distance in the H-bond, because the configurations would not physically differ if the off-center distance were zero. Thus, one can scale from one isomorph to the other using the square of the off-center distance and greatly reduce the total number of free parameters.

In Fig. 11 the heat-capacity data are compared with the calculations of the SUS model. The calculation for DKDP has previously been presented using the same parameters. Parameters were chosen which fit the calorimetric data for DKDP in the region of T/T_c near 0.96, since in this region the value of ΔC is little affected by uncertainties in the choice of C_0 . This calculation is given by the dashed line. The same parameters also give a good fit to the measured spontaneous polarization. The energy parameters were then scaled by the square of the off-center distance and adjusted slightly to better fit the calorimetric data for KDP in the same reduced temperature region. The resulting curve is the solid line in Fig. 11.

The calculation for DKDP is a much better fit to the data than is the calculation of KDP, presumably because the neglect of tunneling is a better approximation for DKDP. For both substances a transition entropy of $0.52R$ is predicted, which is too large to fit the experimental data. The predicted values for the latent heat are 30% too large for DKDP and 580% too large in the case of KDP. In the first case, this may reflect just the difficulties of a mean-field model in satisfactorily accounting for phenomena at phase transitions. In the second case, one may also have serious corrections due to the neglect of proton tunneling.

The calculations of Blinc and Svetina³⁴ are the most comprehensive of any Slater-type theory which incorporates proton tunneling. Because of the complexity of their equations and the multitude of free parameters, no attempt to carry out computations based on their theory was made. The original computations³⁴ show that the deviations between the data and the SUS theory are of the type which can be explained by the inclusion of tunneling. In particular, these results show

³² Y. Takagi, J. Phys. Soc. Japan 3, 271 (1948); 3, 273 (1948).

³³ H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. 133, A165 (1964).

³⁴ R. Blinc and S. Svetina, Phys. Rev. 147, 430 (1966).

³⁵ M. Tokunaga and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 35, 581 (1966).

³⁶ K. K. Kobayashi, J. Phys. Soc. Japan 24, 497 (1968).

that tunneling reduces the value of the heat capacity in the neighborhood of the transition, thus qualitatively explaining the fact that the region of experimentally significant ΔC extends to significantly lower reduced temperatures than is predicted by the SUS theory fitted to the data near T_c . Since tunneling is more important in KDP than in DKDP, one can qualitatively understand why the fit is better for DKDP than for KDP and why the transition entropy is greater in DKDP than for KDP. Further, tunneling calculations of the transition entropy greatly reduce the discrepancy with experiment.

There is, however, one significant discrepancy between the computations and experiment which cannot be resolved simply by the inclusion of tunneling into the SUS theory. This is the observation that there is little, if any, heat-capacity excess over background at reduced temperatures greater than about 1.10. Assuming that this effect is real, and not a result of an incorrect estimate of C_0 , presents a distinct problem to any theory based on a Slater-type model. Two possible resolutions of this problem seem worthy of mention. First, perhaps the assumption of constant energy for the proton configurations is incorrect. Physically, this might be due to the volume changes in the lattice, which are emphasized by the values of the discontinuous volume change given in Table I. The volume changes might change the energies sufficiently to give the observed results. A second, and perhaps more interesting, suggestion might be constructed along the following lines. Recently Kobayashi³⁶ has suggested that the transition in KDP is of a mixed type, in which there is a lattice instability arising because of a coupling of the

proton ordering with the $K^+-PO_4^-$ optical vibration. Evidence for the existence of the resulting "soft mode" has been recently found in Raman scattering data.³⁷ Although the calculation has not been performed, it is possible that, because of the coupling between the proton ordering and the optical mode, the behavior of the heat capacity in the Kobayashi theory is qualitatively different above T_c than is predicted by more conventional theories, which emphasize the role of proton ordering the KDP phase transition. It is to be hoped that further theoretical work will be devoted to this question.

Note added in proof. The observed $\sqrt{\epsilon}$ dependence follows from Eq. (6) if $\gamma^2 K / \delta T_0 \ll 1$. Baumgartner's dielectric data imply that this is the case for KDP. Thus the $\sqrt{\epsilon}$ dependence does *not* imply a failure of the Landau theory.

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³⁷ I. P. Kaminow and T. C. Damen, Phys. Rev. Letters **20**, 1105 (1968).