Schweitzer, J. Appl. Phys. 40, 1099 (1969).

[6] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. 38, 159 (1967).

[7] P. F. Tumelty, Ph.D. thesis (University of Iowa, 1970) (unpublished).

[8] D. B. Fraser, Rev. Sci. Instr. 33, 762 (1962).

[9] J. F. Cochran, C. A. Shiffman, and J. E. Neighbor, Rev. Sci. Instr. 37, 499 (1966).

[10] Princeton Applied Research Corp., Princeton, N. J.

[11] J. S. Rogers, R. J. Tainsh, M. S. Anderson, and C. A. Swenson, Metrologia 4, 47 (1968).

[12] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. 64A, 1 (1960).

[13] An increase in the electronic specific-heat coefficient of dilute $Cu_{1-x}Al_x$ with increasing aluminum concentration has previously been reported by H. Wu and B. A. Green, Jr., Bull. Am. Phys. Soc. 13, 643 (1968); H. Wu, M.S. thesis (Case Western Reserve University, 1968) (unpublished).

[14] E. A. Stern, Phys. Rev. B 1, 1518 (1970).

[15] G. W. Lehman, J. A. Cape, R. E. DeWame, and D. H. Leslie, Bull. Am. Phys. Soc. 9, 251 (1964); B. K. Agrawal, J. Phys. C 2, 252 (1969).

[16] R. M. Nicklow, P. R. Vijayaraghavan, H. G. Smith, and M. K. Wilkinson, Phys. Rev. Letters 20, 1245 (1968).

[17] J. Friedel, Nuovo Cimento, Suppl. 7, 287 (1958).

[18] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[19] V. Jaccarino, J. Appl. Phys. 39, 1166 (1968).

[20] K. C. Brog and W. H. Jones, Jr., J. Appl. Phys. 41, 1003 (1970).

[21] V. Jaccarino and L. R. Walker, Phys. Rev. Letters 15, 258 (1965).

[22] J. W. Loram, T. E. Whall, and P. J. Ford, Phys. Rev. B 2, 857 (1970).

[23] P. E. Bloomfield and D. R. Hamann, Phys. Rev. 164, 856 (1967).

[24] J. Zittartz and E. Müller-Hartmann, Z. Physik 212, 380 (1968).

[25] A. D. Caplin, C. L. Foiles, and J. Penfold, J. Appl. Phys. 39, 842 (1968).

[26] A. D. Caplin, J. Phys. C 3, 4(L) (1970).

[27] F. B. Huck, Jr., W. R. Savage, and J. W. Schweitzer, Phys. Letters 26A, 570 (1968).

[28] D. C. Golibersuch (private communication).

[29] B. M. Boerstoel and W. M. Star, Phys. Letters 29A, 97 (1969).

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Electronic Studies of KH_2PO_4[†]

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The results of electrocaloric studies of the electrical equation of state of KH_2PO_4 in the temperature region within 1 K of the ferroelectric transition are reported. Chief emphasis is given to determination of the spontaneous polarization. A discontinuous polarization jump of $1.87 \pm 0.09\ \mu C/cm^2$ is found at T_c. Several tests of the validity of the phenomenological theory of ferroelectricity, including a noncalorimetric determination of the heat capacity, are made. It is shown that the phenomenological theory provides a good and consistent description of the thermodynamic behavior of KH_2PO_4. No major discrepancies which might be linked to behavior near a phase transition are found. Any possible discrepancies are minor and confined to the temperature region $T_c - T < 0.1$ K. It is shown that a term proportional to P^8 dominates the saturation behavior. Evidence is presented that a portion of the calorimetric anomaly near T_c is not directly related to the temperature dependence of the polarization.

INTRODUCTION

The most widely quoted measurements of the spontaneous polarization of the ferroelectric KH_2PO_4 (KDP) were obtained using the hysteresis-loop method nearly thirty years ago.[1] These measurements, and subsequent ones using the same method,[2,3] indicate that the polarization decreases abruptly, but smoothly, to zero at the transition temperature T_c. This implies that the transition is of second order. Recent dielectric[4,5] and calorimetric[6] data imply that the transition in KDP is of first order.

In addition to providing information concerning the order of the transition, precise polarization measurements, coupled with recent calorimetric data, allow a check of the temperature region of validity of the phenomenological theory (PT) of ferroelectricity. Such a test was the objective of the most recent hysteresis-loop investigation of the polarization in KDP.[3] This study claimed to support the application of the PT, but the results were completely at variance with the calorimetric data.[6,7] Thus, to provide a new test of the applicability of the PT and to reinvestigate the order of the transition, a new investigation of the spontaneous polarization in KDP near T_c has been undertaken.

There are several reasons for regarding hysteresis-loop determinations of the spontaneous polarization near T_c with suspicion. The chief objection of these measurements is the uncertainty in the proper method of interpretation of hysteresis-loop data so as to extract a value for the spontaneous polarization. The traditional method is to perform a linear extrapolation of the saturated portion of the loop to $E=0$. Since the electric susceptibility can be expected to be field dependent, with the strongest field dependence obtaining near T_c, uncertainties are introduced by the resulting nonlinearities. To avoid this problem, Gonzalo[8] and Nazario and Gonzalo[3] chose to interpret the observed value of the polarization at $E=0$ as the spontaneous polarization. The correctness of the determinations obtained by this method depends strongly on the assumption that the sample is saturated during the entire loop. In KDP the loops are observed to be much less square than in other ferroelectrics.[3] This observation may imply that this key assumption is violated. As a quantitative measure of the uncertainty introduced by the question of the proper interpretation of a hysteresis loop, the results of Nazario and Gonzalo are approximately a factor of 3 smaller than those of von Arx and Bantle 1 K below T_c. Additional difficulties beset the proper interpretation of hysteresis-loop data, such as the observed frequency dependence of the results[1] and the question of properly accounting for the electrocaloric effect.[9] However, these questions are relatively less important than the one of interpretation above, which depends in detail upon the domain-wall dynamics of each system under investigation.

There have been several determinations of the spontaneous polarization in KDP which did not make direct use of the hysteresis-loop technique. These studies do not provide suitable evidence for answering the questions raised here. Perhaps the most reliable of such determinations are measurements of the spontaneous strain by x-ray techniques.[10] These measurements were converted into determinations of the spontaneous polarization by comparison with hysteresis-loop measurements made far from T_c. These results extend no closer than 1 K to T_c but indicate that the spontaneous polarization decreases less rapidly with increasing temperature than is indicated by the hysteresis-loop measurements. In fact, these results indicate that a finite polarization jump at T_c may exist. The most recent measurements using nonhysteresis techniques employed pyroelectric determinations of polarization changes with external fields applied.[11] These measurements do not provide good values for the spontaneous polarization near T_c because of problems in interpretation caused by a field- and temperature-dependent susceptibility. The reported values assume constant values of the electrical susceptibility above and below T_c and provide unacceptable results near T_c.

A technique for determining the spontaneous polarization which does not rely on hysteresis techniques and which allows an unambiguous extraction of the effects of applied fields involves measurements of the temperature change resulting from an adiabatic change in polarization $\partial T/\partial P|_S$. We term this temperature change the polarocaloric effect to distinguish it from the closely allied electrocaloric effect, which is the temperature change accompanying the adiabatic application of an external field $\partial T/\partial E|_S$. This allied effect provides information about the temperature derivative of the polarization. The technique which is employed here is a combination of these two effects and will be termed the "polaroelectrocaloric" technique.

Polarization measurements using the polarocaloric effect have been reported for Rochelle salt[12] and triglycine sulfate,[13] but the technique has not yet been applied to KDP. This paper reports the results of polaroelectrocaloric investigations on KDP confined to the temperature range within 1 K of T_c. The methods used in this investigation allow at least one order of magnitude greater precision than previous measurements of this type. The major findings of this study are to demonstrate that no major deviations from the PT can be found and to find a discontinuous polarization jump at T_c. The measurements reported here are demonstrated to be internally consistent and to be consistent with recent calorimetric data.

The thermodynamic foundations of the polaroelectrocaloric technique follow from regarding the entropy S alternatively as a function of temperature T and applied electric field E or as a function of T and polarization P. One then has

$$dS=\frac{\partial S}{\partial T}\bigg|_E dT+\frac{\partial S}{\partial E}\bigg|_T dE\ , \tag{1a}$$

$$dS=\frac{\partial S}{\partial T}\bigg|_P dT+\frac{\partial S}{\partial P}\bigg|_T dP\ . \tag{1b}$$

Considering adiabatic processes and employing the Maxwell relations

$$\frac{\partial S}{\partial E}\bigg|_T=\frac{\partial P}{\partial T}\bigg|_E \quad \text{and} \quad \frac{\partial S}{\partial P}\bigg|_T=-\frac{\partial E}{\partial T}\bigg|_P$$

allows one to obtain the relationships

$$\frac{\partial T}{\partial E}\bigg|_S=-\frac{T}{C_E}\frac{\partial P}{\partial T}\bigg|_E\ , \tag{2a}$$

$$\frac{\partial T}{\partial P}\bigg|_S=\frac{T}{C_P}\frac{\partial E}{\partial T}\bigg|_P\ . \tag{2b}$$

In Eqs. (2), C represents a heat capacity at either constant field or polarization.

Since C_E has been directly measured, determination of $\partial T/\partial E|_S$ can provide a direct determination of $\partial P/\partial T|_E$ which can be simply extrapolated to $E = 0$. However, the polarocaloric effect provides more useful information than does the electrocaloric effect. According to the PT,[14] the elastic Gibbs function for an unstressed ferroelectric can be written

$$G = G_0(T) + \tfrac{1}{2}\alpha(T-\theta)P^2 + \phi(P) , \qquad (3)$$

where $\phi(P)$ is the "saturation function." The saturation function depends on even powers of P higher than quadratic and is assumed to be temperature independent. From Eq. (3) one finds

$$E = \alpha(T-\theta)P + \frac{d\phi}{dP} .$$

Hence it follows that

$$\left.\frac{\partial E}{\partial T}\right|_P = \alpha P .$$

Thus Eq. (2b) can be written as

$$\left.\frac{\partial T}{\partial(P^2)}\right|_S = \frac{\alpha T}{2C_P} , \qquad (4)$$

assuming the correctness of the PT. This relationship predicts that the polarocaloric temperature change should be a linear function of P^2, regardless of any nonlinearities in the relationship between E and P. This then provides an unambiguous method of extracting the spontaneous polarization from polarocaloric measurements.

The polarocaloric measurements also provide a noncalorimetric technique for determining the heat capacity. According to Eq. (4) the slope of a plot of the adiabatic temperature change ΔT as a function of P^2 gives a value for C_P. According to the PT

$$C_E = C_P - \alpha T P \left.\frac{\partial P}{\partial T}\right|_E . \qquad (5)$$

Assuming a value for α, the remainder of the terms on the right-hand side of Eq. (5) can be evaluated from the polarocaloric experiment. More precision results if the derivative is obtained from electrocaloric measurements. Thus the results of a polaroelectrocaloric investigation allow the computation of C_E from noncalorimetric data. Agreement of C_E obtained in this manner with independent calorimetric data supports the use of PT. Finally, comparison of the values of $\partial P/\partial T|_E$ obtained from the electrocaloric measurements with the derivative of the polarocaloric values for P allows a check on the thermodynamic consistency of the measurements and a further, albeit weak, test of the PT.

EXPERIMENTAL CONSIDERATIONS

In concept the polaroelectrocaloric experiment is relatively simple. All that is required is to enclose the sample in an adiabatic shield and to vary a voltage applied to the sample, measuring the voltage across the sample, the charge which flows in the circuit, and the temperature of the sample. In order to ensure a useful precision for the experiment, considerable care must be taken in the realization of this simple concept. A schematic diagram of the experimental apparatus is shown in Fig. 1.

The temperature measuring system and adiabatic shield system are basically those used in previous experiments on KDP,[6,15] although the shield control has been improved since the previous experiments. The adiabatic shield system (A) is enclosed in a vacuum chamber which is immersed in liquid nitrogen. The temperature difference between the shield and the sample (B) is sensed by a differential thermocouple system (C). The output of the thermocouple system is amplified by a Keithly[16] model 148 nanovoltmeter (D). The amplified thermocouple output drives a simple current-control circuit (E). The control circuit incorporates proportional and reset control using a simple logic circuit realized by operational amplifiers. The output of the control circuit supplies the shield heater system (F). This completes the feedback circuit. The control circuit is capable of fully automatic operation and enables the sample temperature to be tracked with maximum deviations of 1 mK. The thermal drift of the resulting system was less than 0.1 mK/h. The sample temperature was sensed using a low-temperature thermistor[17] (G), the resistance of which was sensed by a low-power 37-Hz Wheatstone bridge circuit (H). The temperature of the sample

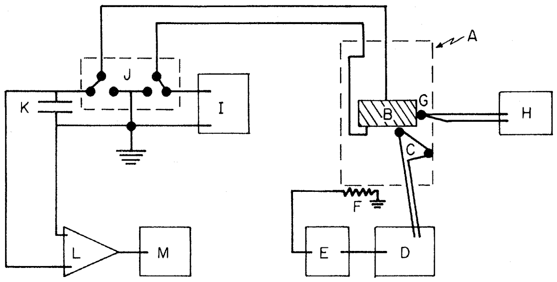

FIG. 1. Schematic representation of an apparatus for the polaroelectrocaloric experiment. The components are A: adiabatic shield; B: sample; C: differential thermocouple; D: dc amplifier; E: shield control circuit; F: shield heater; G: thermistor; H: low-power ac Wheatstone bridge; I: variable voltage source; J: guarded switch; K: reference capacitor; L: electrometer acting as a unity gain amplifier; and M: digital voltmeter.

could be monitored with a precision of approximately 15 μK.

The electrical measurement circuit was driven by a Keithley model 241 power supply (I), the output voltage of which could be set to 0.01 V out of a maximum of 1 kV by panel-mounted switches. The sample was connected to the power supply through a fully guarded switch (J). This switch was constructed using Teflon insulation. All electrical contacts were electrically guarded with guards held at ground potential. Guarding was found necessary to reduce leakage currents to an acceptable level. The electrical measurement circuit was completed by a 0.8-μF polystyrene capacitor (K), the leakage resistance of which was greater than 10^{14} Ω. The voltage across this reference capacitor was determined using a Kiethley 610 BR electrometer (L) which served as a unity gain operational amplifier with an accuracy of 50 parts per million. The output of the electrometer was measured with a Nonlinear Systems model X-1 digital voltmeter (M).[18] The precision of the electrical measuring system exceeded the precision of the measurements, which was slightly better than 0.1%.

The samples used were three single crystals obtained from Clevite Corp.[19] at various times over a period of three years. One was a piece cut from the sample on which heat-capacity measurements[6] had been conducted. This sample was in the form of a plate 2×2×0.6 cm, while the other two were in the form of plates 2.5×2.5×1.3 cm. In all cases the large faces were perpendicular to the c axis, the orientation being checked by x-ray techniques. To test for possible clamping effects of electrodes, each sample had differently prepared electrodes. One sample was provided with thin (300-Å) evaporated gold electrodes while the other two were provided with thicker (1500-Å) evaporated electrodes of gold in one case and tin in the other. The electrodes entirely covered the large faces of the samples. Since all three samples yielded identical results, it was concluded that the presence of electrodes did not affect the measurements.

Electrical connections were made to the evaporated electrodes with No. 40 copper wire bonded with a small amount of indium. Sample preparation was completed by mounting the thermistor, which was attached to a small copper foil, and a small electrical heater to the sample on two of the smaller faces. These attachments were held to the crystal with small quantities of GE 7031 varnish. Finally, the crystal was provided with one end of the differential thermocouple, also held in place with a small amount of varnish, and three nylon threads for suspension. The threads were attached to the sample with small dots of varnish.

All temperatures were measured relative to T_c, which was located by continuously heating the sample until the observation of an isothermal absorption of heat showed that the transition had been reached. The thermistor resistance corresponding to T_c was then noted and values of $d\ln R/dT$ for the thermistor, which had been obtained by calibration against a Pt thermometer, were used to compute $T-T_c$ for all observed resistances.

Data were obtained by first obtaining thermal equilibrium with the sample shorted. Then an electric field of approximately 700 V/cm was applied to the sample. Following this initial application of a field, equilibrium, indicated by both a constant temperature and constant charge on the reference capacitor, was reached in approximately 15 min. After equilibrium had been reached, the field was reduced in approximately 40-V/cm increments. Following equilibrium, which required approximately 5 min, the temperature change and voltage across the reference capacitor were recorded. These data together with the power-supply voltage provided all information necessary for the polaroelectrocaloric measurements. When the field was reduced below 150 V/cm, equilibrium times increased and the data implied that the sample was no longer saturated. When the field was reduced to zero, the polarity was reversed and the procedure repeated. Thus field, temperature, and polarization data were taken over one-half of a hysteresis loop.

During initial application of the voltage the reference capacitor was partly discharged so that the loop would be approximately centered on $E=0$, $P=0$. If this procedure were not followed, a bias, determined by remnant polarization from the previous loop, would be present. The final data were corrected for any remaining bias by requiring that the end points of the loop have opposite values of P.

The resulting data had a reproducibility of slightly better than 0.1%, but had an absolute accuracy of approximately 1% due to uncertainties in the sample dimensions. The precision of the experiment was limited by possible temperature drifts during each quasistatic half-loop and by small leakage currents. The temperature drifts are estimated to be less than 0.2 mK during the approximately 3 h required to complete a set of measurements. Because of superheating and supercooling it was not possible to locate T_c more precisely than ±1.2 mK. However, some data were taken for which the initial temperature was closer than 1.2 mK to T_c, which indicated that the sample had not entered the transition region.

RESULTS AND CONCLUSIONS

Representative examples of the polarocaloric data are shown in Fig. 2. For applied fields above 150 V/cm a very good linear relationship was found to hold between the temperature change ΔT and the square of the polarization measured by the reference capacitor voltage. Such a relationship is predicted by Eq. (4). Extrapolation of the linear curves to $\Delta T = 0$ then provides a value for the spontaneous polarization P_s. Since the data are extrapolated to the starting temperature, the points are labeled by the temperature difference between the initial temperature and T_c. The results of these spontaneous polarization determinations are included in Table I.

The departure from linearity which occurs for fields below 150 V/cm is interpreted as indicating that the crystal was no longer saturated. This interpretation is supported by the previously mentioned observation concerning the equilibrium times and by the behavior of the electrocaloric data. Since data for fields below 150 V/cm then represent the properties of a crystal with a changing domain structure, few data were taken in this field region, and the data which were taken were largely ignored in the processing. Data taken above T_c show a linear extrapolation to $P_s = 0$, as expected, and display no deviation from linearity at low fields. This lends further support to the assumptions on which the extrapolations were made below T_c.

Although it is not apparent from Fig. 2, because of the scale employed, the slope of the linear fit to the data taken above T_c is significantly different from the slope of the fit to the data taken below T_c. Similar behavior is observed in triglycine sulfate.[13] According to Eq. (4) this implies that either the Curie constant (α) or the background heat capacity (C_P) changes at T_c. As discussed below, we favor the hypothesis that C_P changes at T_c.

As shown by Fig. 3, our results for P_s connect reasonably well with DeQuervain's.[10] The agreement of the present work with DeQuervain's can be made even better if it is recognized that his values can be adjusted by a constant factor if his choice of normalization was incorrect. His data were normalized to hysteresis-loop values obtained by von Arx and Bantle about 15 K below T_c. Recent work[11] shows that these values may be slightly

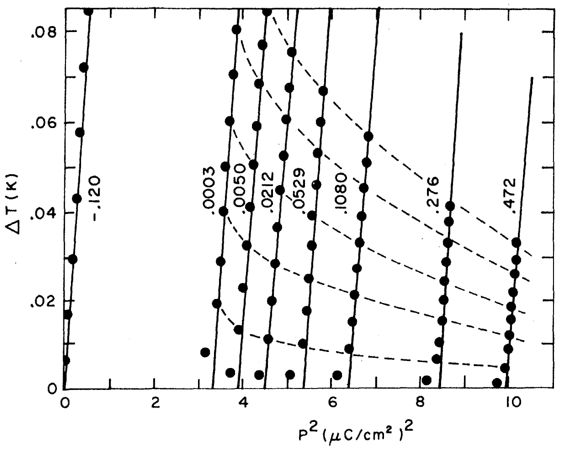

FIG. 2. Representative polarocaloric data showing the adiabatic temperature change from the initial temperature as a function of the square of the sample polarization. The solid lines show the extrapolations to a single domain at $E = 0$ and are labeled by $T_c - T$ at the initial point. The dashed lines show some isochamps.

TABLE I. Thermodynamic properties of a single-domain KDP crystal at $E = 0$ determined from polaroelectrocaloric measurements.

$T_c - T$ (K)	P_s (μC/cm^2)	$\left.\frac{\partial T}{\partial E}\right\|_S$ (10^{-5} K cm/V)	$\left.\frac{\partial P}{\partial T}\right\|_E$ (μC/cm^2 K)
1.129	3.63	2.97	0.513
1.055	3.58	3.04	0.534
0.826	3.45	3.47	0.645
0.693	3.35	3.81	0.741
0.581	3.26	4.36	0.892
0.472	3.16	4.65	1.007
0.360	3.02	5.19	1.22
0.276	2.91	5.93	1.51
0.194	2.76	6.73	1.92
0.154	2.66	7.34	2.27
0.125	2.59	7.84	2.62
0.108	2.54	8.27	2.91
0.0920	2.48	8.62	3.22
0.0810	2.44	8.91	3.50
0.0656	2.38	9.24	3.94
0.0529	2.32	9.69	4.49
0.0338	2.22	10.4	5.64
0.0212	2.13	11.1	6.96
0.0117	2.05	11.9	8.73
0.0050	1.98	12.6	11.17
0.00034	1.83	14.2	19.37

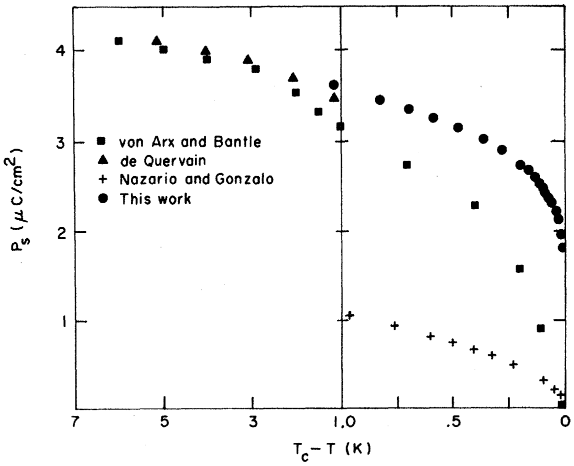

FIG. 3. Spontaneous polarization of KDP as determined by various experiments. The work of von Arx and Bantle and Nazario and Gonzalo employed hysteresis-loop techniques with differing interpretations of the loop. DeQuervain's results refer to measurements of spontaneous strain determined by x-ray techniques. The data from the present work were taken from the polarocaloric measurements.

low.

The present data disagree, especially closer than 1 K to T_c, with the hysteresis-loop measurements. In our view the values reported by Nazario and Gonzalo[3] should be totally discounted since they use fields so low that complete domain alignment cannot be assured, they use frequencies which were shown by von Arx and Bantle[1] to lead to a reduction in the observed value of P_s, and they fail to take any account of a possible field-dependent domain pattern. The values of P_s reported by von Arx and Bantle do not disagree with the current results nearly as badly as do those of Nazario and Gonzalo, but these values do go to zero at T_c while the present results indicate a value of $P_s(T_c) \equiv P_0 = 1.87 \pm 0.09\ \mu C/cm^2$. In our view the chief criticism of the von Arx-Bantle results near T_c is that they do not take proper account of the nonlinearities in the relationship between P and E which occur immediately above T_c. Application of the von Arx-Bantle method of analysis in the presence of such nonlinearities will lead to nonvanishing of P_s *above* T_c. Since their value for T_c was apparently established as the temperature at which P_s vanished, we suspect that they chose too high a temperature for T_c. Hence, values of P_s reported near T_c in this work are open to question.

A log-log plot of the polarization data showed that the expression

$$P_s \propto (T_c - T)^{0.168}$$

fit the data very well for $T_c - T > 0.02$ K. In terms of the PT, this observation implies that the P^8 term in $\phi(P)$ dominates near T_c. It has been previously recognized that the P^4 term makes a small but important contribution,[20,21] but previous attempts to construct $\phi(P)$ showed, or assumed, a large P^6 contribution. Guided by our experimental observations we attempted to find an expression for $\phi(P)$ which would account for a first-order transition and the polarization data containing only P^4 and P^8 terms. Assuming such a form for $\phi(P)$ allows a two-parameter fit to the temperature dependence of the polarization to be found in terms of the equation

$$P_s^6 - \tfrac{3}{4}P_0^4 P_s^2 + \frac{P_0^6(T-\theta)}{2(T_c-\theta)} = 0\ . \tag{6}$$

In Eq. (6) the two parameters are P_0 and θ, the Curie-Weiss temperature (or $T_c - \theta$). These two parameters were varied to obtain the best fit to the polarization data. The best fit is shown in Fig. 4. The fit could be improved near T_c by including a small P^6 term. If one attempts to fit the entire temperature dependence of the polarization one needs to include terms of higher order than P^8. Neither of these refinements seems significant so far as our main points are concerned, so they were not pursued. The fit uses the parameters $P_0 = 1.872\ \mu C/cm^2$ and $T_c - \theta = 0.012$ K. Of these two parameters, only $T_c - \theta$ is suitable for comparison with other work. The most suitable experiments for directly determining $T_c - \theta$ are measurements of the dielectric constant performed with considerable temperature resolution. From the studies of this type which have been carried out[4,22,23] one can only conclude that $0 \leq T_c - \theta \leq 0.05$ K.

If one assumes a value for α, one can calculate the coefficients of a power-series expansion of $\phi(P)$. We have assumed the value of α given by Craig's work[4] and find $\beta = -4.4 \times 10^{-12}$ and $\delta = 2.96 \times 10^{-27}$, where cgs units are implied. β is the coefficient of the P^4 term and δ is the coefficient of the P^8 term. The negative value of β implies a first-order transition. These coefficients differ from values reported previously.[20,21] The set obtained by Reese[20] from an analysis of saturation data obtained by Baumgartner[22] has problems of internal consistency, although it provides a fair representation of the heat capacity. This set was chosen to fit the rapidly varying portion of Baumgartner's saturation function. If another portion of the function had been emphasized in the fitting, a very different set, differing even in the sign of β, could have been obtained. This raises questions concerning the internal consistency of the Baumgartner data. The set obtained by Gladkii *et al.*[21] implies a negative value of β, but suffers because it is based on a value of α almost 50% different from the value obtained by many other investigators.

The ability to fit the present polarization data with a two-parameter fit of the form dictated by the PT is one argument for the applicablity of the PT to KDP near T_c. Stronger arguments leading to this same conculsion are based on comparison

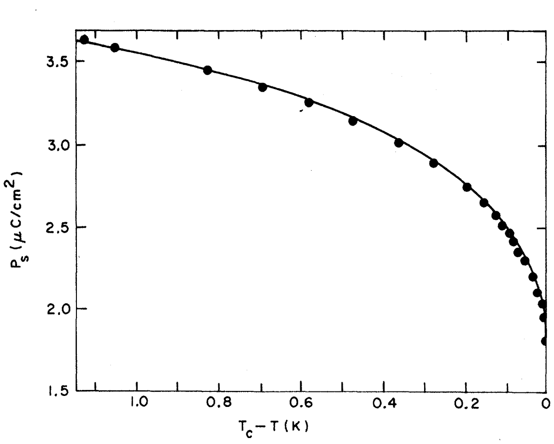

FIG. 4. Comparison of the present spontaneous polarization data with two-parameter fit obtained using Eq. (6). This equation is obtained from the phenomenological theory of ferroelectricity assuming only P^4 and P^8 terms in the saturation function.

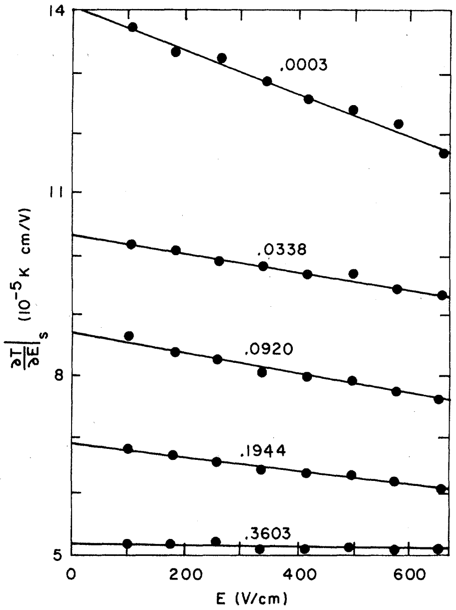

FIG. 5. Field dependence of the electrocaloric coefficient for KDP. The curves are labeled by $T_c - T$ with T referring to the $E = 0$ temperature.

of the polarocaloric data with electrocaloric and calorimetric data. These arguments will now be discussed.

For fields in excess of 150 V/cm the electrocaloric temperature change was substantially proportional to the field change. However, with the precision available in the present experiment the effects of a small negative value for $\partial^2 T/\partial E^2|_S$ could be distinguished. This is illustrated by the representative data shown in Fig. 5. These data show the local slope $\partial T/\partial E|_S$ obtained from the electrocaloric data as a function of applied field. Although deviations from the assumption of a field-independent second derivative were observed, these deviations are on the order of the precision of the data. Thus a linear fit was all that was attempted. The values of $\partial T/\partial E|_S$ which characterize a single-domain crystal at $E = 0$ were obtained by straight-line extrapolation and are given in Table I.

The electrocaloric data, extrapolated to zero field can be used to compute $\partial P/\partial T|_{E=0}$ using Eq. (2a). A test of the internal consistency of the data and a test of the PT, which was used in a very weak form to obtain P_s, is the agreement between dP_s/dT and the electrocaloric data. Such a comparison is shown in Fig. 6. For the purpose of this comparison we have differentiated the PT fit to the polarization data, which is that shown in Fig. 4. Although the agreement displayed in Fig. 6 is impressive, even better agreement is possible since the small deviations which occur near $T_c - T = 0.1$ K are a result of a failure of the two-parameter fit to represent faithfully the polarization data. This test then gives confidence in the internal consistency of our data and in the consistency of the data with the PT.

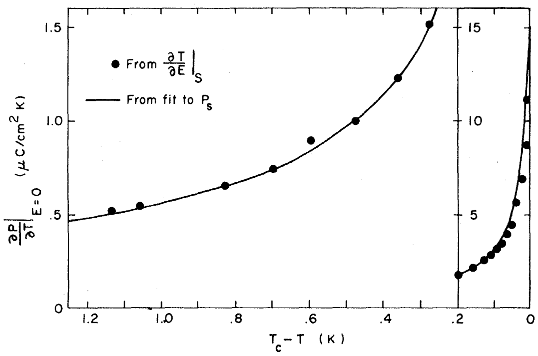

FIG. 6. Comparison of the temperature derivative of the spontaneous polarization in KDP obtained from electrocaloric data with the derivative of the phenomenological theory fitted to the spontaneous polarization data derived from the polarocaloric measurements.

A more stringent test of the consistency of our data with the assumptions of the PT comes upon comparison of the present results with calorimetric data. As discussed previously, polaroelectrocaloric measurements allow a noncalorimetric determination of C_E. We shall continue to work at $E = 0$, considering it to be the most interesting field value.

Using Craig's value for α, we have the C_P from the slope of plots of ΔT vs P^2. C_P so calculated includes not only that portion of the heat capacity of the crystal not directly associated with the temperature dependence of the polarization but also that of the addenda. Above T_c, $C_E = C_P$ for $E = 0$. Thus, the addenda heat capacity was evaluated by comparing the value of C_P obtained from data taken above T_c with previous calorimetric data. The re-

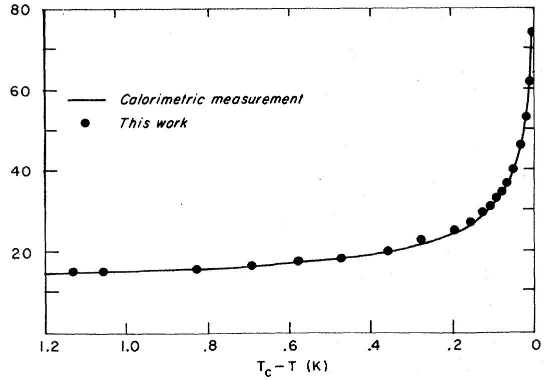

FIG. 7. Comparison of the specific heat at $E = 0$ for KDP as obtained from the polaroelectrocaloric data with the calorimetric measurements reported in Ref. 6.

sulting addenda heat capacity fell within the range of values estimated on the basis of its known composition. Subtracting this value of the addenda heat capacity should then yield a value of C_P which characterizes the crystal only. Using this value of C_P, which was temperature independent below T_c within the scatter of the data, $C_{E=0}$ was calculated using Eq. (5) with P taken from polarocaloric measurements and $\partial P/\partial T|_{E=0}$ taken from electrocaloric measurements. The results of this computation are compared with calorimetric determinations of $C_{E=0}$ in Fig. 7. The agreement must be considered excellent. A similar point of agreement comes upon comparison of the PT prediction of the latent heat obtained from P_0. The PT value is 42.9 ± 4.3 J/mole, which is in excellent agreement with the calorimetric value of $46.2^{+4.0}_{-6.0}$ J/mole.

One interesting feature of the heat capacity comparison has already been alluded to: A larger value was found to characterize C_P below T_c than above. When account of the addenda heat capacity is taken we find that $C_P/R = 9.39 \pm 0.3$ below T_c. The most remarkable feature of this observation is that C_P is about R greater below T_c than the measured heat capacity immediately above T_c. This implies that a portion of the calorimetric anomaly in KDP is not *directly* connected with the temperature dependence of the polarization. An alternative to assuming that C_P changes at T_c is to assume a change in α. If this assumption is made, the good agreement between C_E determined from the polaroelectrocaloric measurements and determined by calorimetric techniques is spoiled. Thus, we favor the assumption of a change in C_P. Acceptance of this hypothesis explains why the PT estimate of the total transition entropy in KDP is too low, $0.35R$ as compared with the observed value $0.40R$. This discrepancy results since the PT estimate refers only to the portion of the anomaly directly associated with the polarization and we see here evidence for an additional contribution.

The nature of the data on which this report is based is such that considerably more information concerning the electrical equation of state of KDP within 1 K of T_c could be extracted. However, since one of the chief conclusions of our work is to find that the PT gives a good description of KDP in this temperature range, such an analysis would be redundant. Thus, we have refrained from reporting such additional data.

In conclusion we find that the ferroelectric transition in KDP exhibits a discontinuous jump in polarization at T_c. More significantly, we find that the phenomenological theory of ferroelectricity provides a good and consistent description of the thermodynamics of KDP: We find no evidence of major discrepancies which can be ascribed to "critical-point phenomena." If there are discrepancies, they are minor and occur in the temperature region $T_c - T < 0.1$ K. We find that in the temperature range explored here the saturation function is dominated by the P^8 term and that the P^6 term plays so subordinate a role that it may be neglected. Finally, evidence has been presented which implies that a portion of the calorimetric anomaly observed in KDP is not directly connected with the temperature dependence of the polarization.

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[1] A. von Arx and W. Bantle, Helv. Phys. Acta 16, 211 (1943).

[2] R. E. Oettel, M. S. thesis (University of Washington, 1964) (unpublished).

[3] I. Nazario and J. A. Gonzalo, Solid State Commun. 7, 1305 (1969).

[4] P. P. Craig, Phys. Letters 20, 140 (1966).

[5] S. Tsunekawa, Y. Ishibashi, and Y. Takagi, J. Phys. Soc. Japan 27, 919 (1969).

[6] W. Reese, Phys. Rev. 181, 905 (1969).

[7] B. A. Strukov, M. Amin Soliman, and V. A. Kopsik, J. Phys. Soc. Japan Suppl. 28, 207 (1970).

[8] J. A. Gonzalo, Phys. Rev. 144, 662 (1966).

[9] W. Reese, Phys. Rev. 182, 646 (1969).

[10] M. DeQuervain, Helv. Phys. Acta 17, 509 (1944).

[11] J. Azoulay, Y. Grinberg, I. Pelah, and E. Wiener, J. Phys. Chem. Solids 29, 843 (1968).

[12] G. G. Wiseman and J. K. Kuebler, Phys. Rev. 131, 2023 (1963).

[13] B. A. Strukov, Phys. Status Solidi 14, K135 (1966).

[14] A detailed exposition of the phenomenological theory of ferroelectricity can be found in such books as J. C. Burfoot, *Ferroelectrics* (Van Nostrand, Princeton, N. J., 1967), or E. Fatuzzo and W. J. Merz, *Ferroelectricity* (North-Holland, Amsterdam, 1967).

[15] W. Reese and L. F. May, Phys. Rev. 162, 510 (1967).

[16] Kiethley Instruments Corp., Cleveland, Ohio.

[17] Type RL 10X04, Keystone Carbon Co., St. Marys, Pa.

[18] Non-Linear Systems, Inc., Del Mar, Calif.

[19] Clevite Corp., Electronic Research Div., Cleveland, Ohio.

[20] W. Reese, Solid State Commun. 7, 969 (1969).

[21] V. V. Gladkii, I. S. Zhelnder, and E. V. Sidnenko, J. Phys. Soc. Japan Suppl. 28, 206 (1970).

[22] H. Baumgartner, Helv. Phys. Acta 23, 651 (1950).

[23] E. M. Brody, Ph. D. thesis (Johns Hopkins University, 1969) (unpublished).