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Studies of Phase Transitions in Order-Disorder Ferroelectrics. II. Calorimetric Investigations of KD_2PO_4†

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Calorimetric measurements on KD_2PO_4 have been conducted, and the transition is found to be first order with an entropy change at T_c of $(0.2407\pm0.0016)R$. The entropy change associated with destruction of the polarization from 0°K to T_c is found to be $(0.4234\pm0.0071)R$. It is shown that a mean-field theory of the type proposed by Silsbee, Uehling, and Schmidt can give a good account of the heat capacity and polarization to within about 1°K of T_c, although the latent heat and entropy are not predicted satisfactorily, presumably because of the breakdown of the mean-field approximation close to the transition. Below T_c the divergence in the heat capacity may be argued to be logarithmic in the region closer than 1° to T_c, or to be as $1/(T_c-T)^{1/2}$ in the region $T_c-2°<T<T_c-0.2°$. Arguments are offered in favor of the logarithmic divergence.

I. INTRODUCTION

The importance of the establishment of long-range order of the hydrogen-bond network in the ferroelectric transition of potassium dihydrogen phosphate and its isomorphs is by now well established.[1,2] As a rather dramatic manifestation of the role of the hydrogen-bond system in the transition, one can cite the shift in critical temperature from about 121°K to about 220°K[3] which occurs on deuteration. Recently, high-resolution calorimetric measurements were made in a study of the phase transition of KH_2PO_4 (KDP) which showed the transition to be second order, or at least "nearly so" in the sense that the latent heat, if any, was small.[4] This work is an extension of the previous study to the deuterated isomorph KD_2PO_4 (DKDP) in which it is found that the transition is of first order and that a classical, mean-field theory gives rather satisfactory account of the thermodynamic properties except within a few degrees of the transition.

The crystal structure of KDP-type crystals in the paraelectric phase is a tetragonal, "diamond-like" structure in which each phosphate group is surrounded by a tetrahedron of other phosphate groups, with hydrogen bonds connecting phosphate groups. In the ferroelectric transition, the unit cell undergoes a small shear (about $\frac{1}{2}$°) lowering the symmetry and causing displacements of the phosphate groups and potassium ions sufficient to account for the observed spontaneous polarization.

The potential well for the hydrogens has a double minimum, leading to two possible off-center hydrogen positions. Slater[5] first recognized that the ordering of the hydrogens within these two possible potential minima plays a key role in the transition. In this paper, we will adopt the notation of Silsbee, Uehling, and Schmidt (SUS).[6] In such a discussion the arrangement in which both "lower" (or "upper") hydrogens are close to a given phosphate group is taken to be the lowest energy state, taken as zero energy. The other four configurations in which exactly two hydrogens are associated with each phosphate are taken to have an energy ϵ_0. At this point we should note, following SUS, that if the potential minimum were not off center there would be no difference between the configurations labeled 0 and ϵ_0, so that it is reasonable to take ϵ_0 as related to the off-center distance. Since the off-center distance is greater in the deuterated isomorph,[7] we expect ϵ_0 for KDP to be smaller than for DKDP (in fact, if we scale by the ratio of the square of the off-center distances, the ratio is 0.56).[8]

In the original Slater theory these configurations were assumed to be the only possible ones. However, Takagi[9] generalized the Slater model by the introduction of configurations with one or three hydrogens were in the minima closest to a given phosphate group (corresponding to HPO_4^- or $H_3PO_4^-$ groups) with energy ϵ_1. It is possible to introduce configurations in which zero of four hydrogens are associated with a given phosphate group, but these are expected to correspond to very high energies and contribute very little and, in addition, contribute nothing new to the theory,[10] and so will be ignored. The inclusion of these configurations can lead to a transition of either first- or second-order depending on the ratio ϵ_1/ϵ_0. Through an analysis of the temperature dependence of the nuclear-magnetic relaxation Schmidt and Uehling[11] deduce that ϵ_1/k is approximately 900°K for DKDP. The Takagi theory was generalized further by SUS through the introduction of a mean-field term in the Hamiltonian

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[1] W. Kanzig, in *Solid State Physics*, edited by F. Sietz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 1.

[2] F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Co., New York, 1962).

[3] R. M. Hill and S. K. Ichiki, Phys. Rev. **130**, 150 (1963).

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

[5] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[6] H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. **133**, A165 (1964).

[7] S. B. Garret, U.S. Atomic Energy Commission, Oak Ridge National Laboratory Report No. ORNL-1745, 149, 1954 (unpublished).

[8] R. Blinc and S. Svetina, Phys. Rev. **147**, 430 (1966).

[9] Y. Takagi, J. Phys. Soc. Japan **3**, 271 (1948); **3**, 273 (1948).

[10] G. Shirane and T. Oguchi, J. Phys. Soc. Japan **3**, 274 (1948).

[11] V. H. Schmidt and E. A. Uehling, Phys. Rev. **126**, 477 (1962).

βp^2, where p is the normalized polarization and β is a parameter. Using standard statistical techniques, they then found an expression, which must be evaluated numerically, for the free energy, and hence for all other thermodynamic functions. The theory has three parameters, ϵ_0, ϵ_1, and β. However, one of these has been determined by the resonance results. By matching the observed transition temperature (which is primarily determined by ϵ_0) the number of free parameters in the theory can be reduced to one. In the discussion of our experimental results below, we will find that this theory is capable of a rather satisfactory prediction of the thermodynamic properties of DKDP, except in the neighborhood of the transition temperature, with one free parameter.

In the neighborhood of the transition temperature the heat capacity rises more rapidly and the polarization falls off more quickly than predicted by the SUS theory. This type of behavior is characteristic of the failure of all theories of the mean-field type in the neighborhood of the phase transition and is thought to represent the inability of a theory of this type to cope with correlations of increasing range as the phase transition is approached. An analysis of the heat-capacity divergence below T_c shows that it is possible, as in the case of KDP,[4] to argue either for a sharp, logarithmic divergence or a divergence as $1/(T_c-T)^{1/2}$ with rather severe rounding.

II. EXPERIMENTAL

The apparatus and techniques employed in this study are similar to those employed previously,[4] with a few significant changes, discussed below. The thermometer employed in the present work was a thermistor for which $(1/R)dR/dT$ was approximately 0.064/°K at the transition temperature of DKDP (YSI Model 44002, Yellow Springs Instruments). The temperature could then be measured to a precision of about 50 μ°K. The thermistor was calibrated against the same Pt thermometer employed previously. The temperature bath outside the calorimeter was "dry ice" and acetone for the present experiment. Because of the much reduced radiation resistance at these higher temperatures, the adiabatic shield system used previously was improved by the fabrication of a double shield system so that the thermal isolation in the present experiment was about the same as before.

A major improvement in technique was to employ a single-crystal sample. The sample was a 12.65 g piece cut from a larger crystal supplied by Isomet Corporation and stated to have a deuteration level of at least 97%. For the bulk of the measurements the crystal was wrapped with approximately 1 g of Cu foil, held in place with a small amount of GE 7031 varnish, so as to promote thermal transfer. The time required for equilibration following a heat input was approximately 3 min.

In addition to the measurements on the crystal "shorted" by the Cu foil, a series of measurements was taken in which the Cu foil was not used, so that the surface of the crystal was free of electrical shorts. For the measurements on the shorted crystal, the addenda correction was measured in a separate series of measurements, but in the case of the "free" crystal no addenda measurements were made. In this case an addenda correction was made by matching the heat capacity of the free crystal to that of the shorted 10° above and below the transition. There was no significant difference between the measurements on the free and shorted crystals, except for a temperature shift of about 0.09°K which was traced to a change in calibration of the thermistor and verified as such by recalibration.

When measurements far from T_c were being made, temperature increments of between 0.5 and 1.5°K were employed for the most part. In the neighborhood of T_c much smaller temperature steps were taken, typically from 0.05 to 0.03°K. At the edge of the latent-heat anomaly, some very small temperature increments of about 2 m°K or less were taken, but these data do not provide the bulk of the data reported here. Over all, the data have a precision of about 0.5%, except for the smallest increments for which it is slightly less precise, and an accuracy of about 1.5%. Latent-heat determinations were made by application of heat in one or two steps with heat-capacity data used to correct the data for temperature steps to the edge of the anomaly. In no case did the correction amount to that corresponding to more than a 0.02°K correction in temperature, with the correction more often being on the order of 0.007°K.

III. RESULTS AND DISCUSSION

The heat-capacity data obtained in this study are presented in Table I, in which the measurements have been averaged over temperature intervals of sufficiently small size so as not to distort the temperature dependence. The data from a single experimental run in the interval between 219 and 220°K are displayed in Fig. 1. Here we see the sudden increase in the heat capacity which takes place in the interval between 219.95 and 219.98°K. We take this sudden and discontinuous rise to represent the entering of a region of a first-order phase transition spread over the interval of about 0.03°K. In this interval the apparent heat capacity rises by several orders of magnitude, with the bulk of the enthalpy change occurring in an interval whose width is approximately 0.005°K centered on 219.962°K. We have attempted to fit the heat-capacity results obtained for points which had an initial and/or final temperature in the range 219.95–219.98°K to some simple forms, such as the Gaussian distribution,[12] without success. In any case, without inquiring as to

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[12] See, e.g., T. Yamamoto, O. Tanimoto, Y. Yasada, and K. Okada, Natl. Bur. Std. (U.S.) Misc. Publ. **273**, 86 (1966).

TABLE I. Heat capacity of KD_2PO_4. Except near T_c, the points represent averages of several points over an interval sufficiently small that there is little significant change in the heat capacity across the interval. Some data, including the points shown in Fig. 1, for which the initial and/or final temperatures fall within the "latent-heat" region are included and designated with asterisks. The proper interpretation of these data is not clear, and they may not be representative of data taken on other DKDP samples, although they were reproduced reasonably well (better than 10%) on other runs on the same sample. These points are included primarily for reference.

T(°K)	C(J/mole°K)	T(°K)	C(J/mole °K)	T(°K)	C(J/mole °K)
239.20	101.0	*219.959	52000	218.08	132.6
235.75	97.8	*219.980	242	217.70	127.1
232.92	98.6	*219.981	228	217.25	122.1
231.03	98.6	*219.990	125	216.80	118.6
230.04	98.7	219.929	248.6	216.32	115.1
228.04	98.5	219.896	236.3	215.59	111.1
226.57	97.2	219.869	225.7	214.50	106.4
225.14	97.6	219.863	225.7	213.57	103.7
223.80	97.2	219.839	220.6	212.48	101.4
222.77	98.2	219.793	213.1	211.23	98.7
222.03	98.0	219.741	204.0	209.16	95.9
221.64	97.9	219.682	198.0	207.03	93.7
221.33	98.4	219.610	190.1	204.90	91.9
220.978	98.7	219.510	181.5	202.91	90.9
220.769	99.0	219.431	173.4	200.68	89.7
220.572	98.3	219.318	166.2	199.22	89.4
220.406	98.6	219.216	163.2	197.14	88.0
220.199	98.9	219.107	156.8	194.82	86.7
220.068	100.0	219.00	153.7	192.84	85.8
*219.940	788	218.85	149.4	190.86	85.2
*219.948	1200	218.57	142.7	188.85	84.3
*219.954	2260	218.32	136.4	186.83	83.5
*219.957	2420				

the causes of the spread in transition temperature indicated by these observations, we can report that this anomalous region corresponds to a first-order transition with a latent heat of 440.3±2.8 J/mole and corresponds to an entropy change at the phase transition of $(0.2407\pm0.0016)R$. The bulk of the uncertainty quoted here represents difficulty in assessing the boundaries of the "latent-heat" region. The above measurements represent the average of five independent determinations. Our observation supports the conclusion drawn by Bjorkstam[13] that the phase transition in DKDP was first order. His conclusion was based on the observation of the coexistance of deuteron-magnetic resonance spectra characteristic of both the paraelectric and ferroelectric phases. In passing, we might mention that it was easy to cause a superheating of about 0.01°K or more if the transition was approached too rapidly.

In order to make further progress in the analysis of the data one needs some method by which to subtract the contribution to the total heat capacity due to lattice vibrations, C_G. This procedure is certainly the most difficult part of the entire analysis and the one most subject to criticism, but a step which must be completed before further analysis can be attempted. If this step is carried out incorrectly the remaining conclusions are subjected to corresponding doubt. In this work we have adopted the following technique for estimating C_G. There exist quite good measurements of the heat capacity of KDP over this temperature interval,[14] which, if theories of the Slater type are correct, consist of a lattice contribution plus a small contribution from disordering in the hydrogen-bond system. We have assumed that: (1) The lattice contributions in KDP and DKDP are identical, (2) that the contribution of hydrogen-bond-system disordering can be calculated using the SUS theory, and (3) that the two parameters needed for this calculation can be scaled from the parameters used in the analysis of DKDP given below. These points and their uncertainties will be discussed below in the reverse order.

To form an estimate of the parameters needed to calculate the disordering contribution to the heat capacity of KDP, we have taken ϵ_1 to be the same for the two isomorphs and ϵ_0 to be 0.56 of that for DKDP,

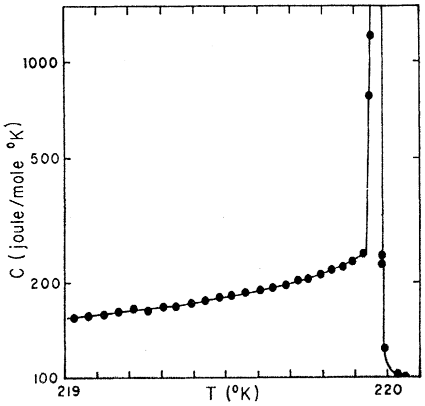

FIG. 1. The heat-capacity points obtained from a single pass through the ferroelectric transition. This figure illustrates the sudden discontinuity characterizing the "latent-heat" region and shows its extent.

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[13] J. L, Bjorkstam, Phys. Rev. **153,** 599 (1967).

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

in accord with a scaling by the square of the off-center distance of the well, as suggested by Uehling (see Ref. 8). We deduce below two possible values of ϵ_0 for DKDP by fitting the data under two possible assumptions, but it is fortunate that the difference between these two values only makes a difference of 0.05 J/mole °K in the disordering heat capacity, which is negligible compared to the total heat capacity, which is of the order of 100 J/mole °K, and to experimental errors. We might note that either of the choices of parameters which can be made will lead to a transition temperature for KDP in the neighborhood of the observed value. One does not expect a theory of the SUS type to hold exactly for KDP, for if it did, any reasonable choice of parameters, such as that above, would lead to a transition in which the spontaneous polarization immediately jumps nearly to its final value and the transition would not be of second order, both in contradiction to experiment. To avoid these contradictions, a modified theory of the tunneling type is required.[8] However, such theories differ but little from the SUS theory far from the transition temperature, and we are far from the transition temperature of KDP for our estimate of C_G.

The first assumption is subject to at least two separate types of criticism which are independent of any points raised above. First, one can not expect the lattice-heat capacity to be completely independent of deuteration, although this will certainly have to be nearly true at sufficiently high temperatures. Second, one may object that the measured heat capacity for KDP refers to the paraelectric (tetragonal) phase throughout while the data for DKDP refer to the ferroelectric (orthorhombic) phase below 220°K. Thus one might expect that our estimate should be better for the paraelectric phase than for the ferroelectric phase. However, because of the small distortion one can hope that this effect is small. In addition, one might invoke an unknown lattice-ordering coupling which might be strong in the neighborhood of the transition and which might completely invalidate the analysis on that region.[15]

Figure 2 shows the relationship between the calculated lattice contribution and the total heat capacity, and indicates that our assumptions at least lead to a plausible curve which might be drawn simply on the criterion of a simple smooth curve under the data. In view of the uncertainties noted above, it is probably optimistic to assume that the lattice contribution is known to within 1%, particularly in the ferroelectric phase, and particularly in the immediate neighborhood of the transition. However, in this regard we note that the total heat capacity in the neighborhood of the transition is so large that a relatively large uncertainty in C_G results in only a small percentage uncertainty in $C-C_G$.

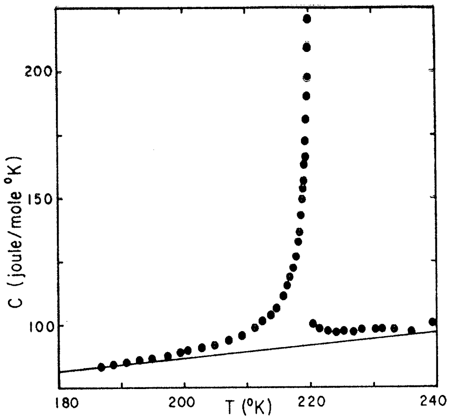

FIG. 2. The heat capacity of DKDP is shown as a function of temperature and in relation to the lattice-heat contribution deduced by subtracting from the heat-capacity data for KDP of Stephenson and Hooley a contribution calculated using the SUS theory with ϵ_0 scaled from the value needed to fit the latent heat DKDP. The lattice contribution is shown by the solid line.

Using the estimate of C_G obtained above, we calculate a total entropy change associated with the ferroelectric transition from 0° to T_c as $(0.4234\pm0.0071)R$, where the uncertainty represents the uncertainty in the experimental data only. As we can see, over half of the entropy change occurs at the critical point. This value for the entropy is considerably larger than that deduced by Bantle,[16] and our heat-capacity results also differ considerably from this. We believe that this discrepancy has at least two sources: First is the poor experimental technique employed in Bantle's work in which heat capacity was deduced from a continuous heating over about a 50°K interval in but 80 min, and second is the possible dubious quality of the crystals employed by Bantle, as evidenced by the double maxima in heat capacity in his observations. Before leaving this point we might note that the entropy change from 0° to T_c is but slightly larger than that found for KDP[4] $(0.405R)$ in which, however, a considerably more naive estimate of C_G was made.

If reliable heat-capacity data for DKDP were available in the temperature range below 125°K, one could, of course, reverse the technique employed above to obtain an improved estimate of C_G for KDP using the measured C for DKDP [since as indicated by Figs. 2 and 3(a) the heat-capacity DKDP is almost entirely due to C_G below about 180°K]. Outside of this temperature interval the difference between C and C_G for KDP and DKPD is small, about 5% of the total heat capacity, so that good accuracy of the heat-capacity data are needed if comparisons are to be meaningful. We have already performed some preliminary heat-capacity measurements on DKDP in the temperature range 80–185°K which indicate that the above mentioned estimate of C_G for KDP, while substantially correct, can be improved. However, these measurements are not yet completed and will be reported together with a re-examination of the transition in KDP using a single-crystal sample.

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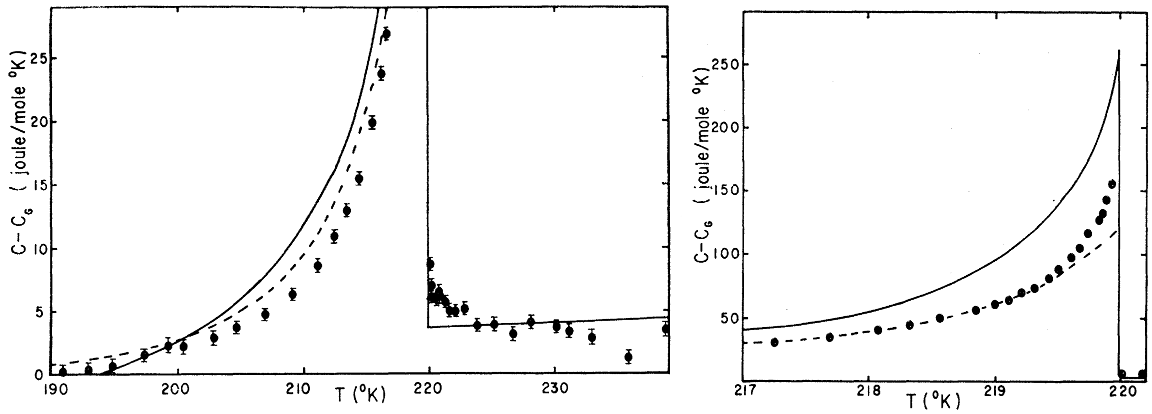
[15] J. F. Nagle and M. E. Fisher (to be published).

[16] W. Bantle, Helv. Phys. Acta **15**, 373 (1962).



(a) (b)

FIG. 3. The difference between the total heat capacity and the lattice heat capacity, $C-C_G$, is compared with calculations of the SUS theory. The solid line represents the parameter set required to match the latent heat ($\epsilon_0/k=102$°K, $\epsilon_1/k=900$°K, $\beta/k=30.7$°K) while the dashed line represents a parameter set choosen to fit the heat capacity between 217 and 219°K ($\epsilon_0/k=94.3$°K, $\epsilon_1/k=900$°K, $\beta/k=35.6$°K). The error bars are chosen to represent an uncertainty of 0.5% in the original data. No indication of possible uncertainties coming from the estimate of C_G is given, but the uncertainty is probably at least twice as large as the assigned error bars.

Let us now turn to a comparison of our results with the SUS theory. We take as fixed the value of ϵ_1 obtained from the resonance measurements and the transition temperature. We then have one free parameter which we shall take as ϵ_0, adjusting β so as to keep T_c fixed at 219.962°K. One way of choosing this additional parameter is to require that the theory match the latent heat. This choice gives us $\epsilon_0/k=102$°K and $\beta/k=30.7$°K. This may not be the best choice for the parameter, because one expects theories of the mean-field type to break down in the neighborhood of the transition temperature; we have, therefore, also investigated the choice $\epsilon_0/k=94.3$°K and $\beta/k=35.6$°K, chosen to produce a fit to the heat-capacity data between 217 and 219°K. Both of these parameter sets are different from that deduced by SUS, who attempted to fit measurements of the spontaneous polarization with parameters which gave a transition of second order. The data are then compared with the predictions of the SUS theory in Fig. 3. The data shown are those tabulated in Table I with the error bars assigned on the basis of an 0.5% uncertainty in the original data. Not shown is an indication of the uncertainties due to the choice of C_G. Both choices give at least qualitative success, with the quantative success above T_c giving us considerable encouragement that our choice of C_G is a correct one. The second set of parameters gives a much better fit to the heat-capacity data, as might be expected on the basis of the method of choice. However, this set of parameters predicts an entropy change at T_c of $0.3131R$, about 30% higher than the observed value. Also, it might be pointed out that both parameter choices lead to a value of the entropy of the paraelectric state at T_c of $0.52R$, which is about 23% larger than the experimental value. We take this failure of the SUS theory to be symptomatic of the generic failure of theories of the mean-field type near the critical point. In this regard, we see that the heat-capacity rises above the calculated curve in the region $|T-T_c|<1$°K as in the usual failure of mean-field theory to account for phenomena near the phase transition.

In Fig. 4 we compare the SUS calculations of the spontaneous polarization with the measurements of Hill and Ichiki.[17] For this comparison we have taken the value of the saturation polarization at $T=0$ to be 5.95 μC/cm^2, a value guided by a desire to match the calculated and experimental curves at low tempera-

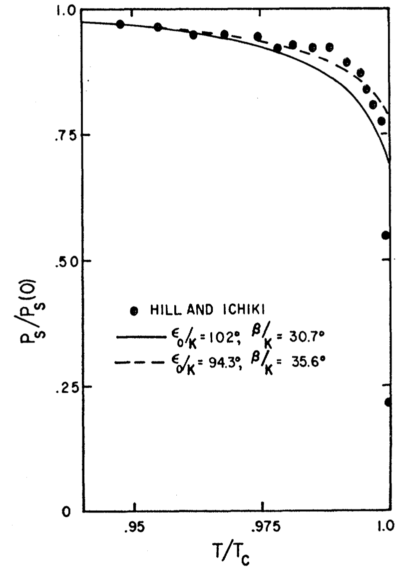


FIG. 4. A comparison of the spontaneous polarization divided by its final value at 0°K, which was taken to be 5.95 μC/cm^2 to match the calculations at low temperatures, against normalized temperature. The data are taken from Ref. 17. The calculated curves were obtained using the SUS theory and the same parameter sets as the calculated curves in Fig. 3.

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

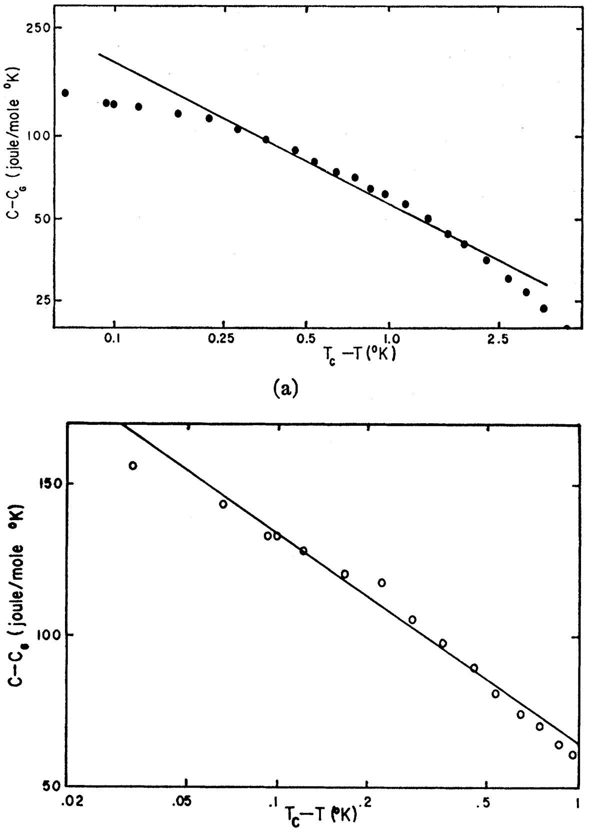
tures. We see that the set of parameters which gives the best fit to the heat capacity also gives the best fit to the spontaneous polarization.

It is perhaps worth mentioning that the present calculations do not agree at all well with the older data of Zwicker and Scherrer,[18] which were obtained using an indirect method. Because it is these data to which SUS fit their calculations, it is not surprising that the value of the parameters ϵ_0 and β deduced by SUS are considerably different from those employed here.

We choose to interpret the two points taken within 0.1°K of the state of zero polarization to be non-equilibrium points on a sample partly in the ferroelectric and partly in the paraelectric phases. If this is not so, and these points are thermal-equilibrium measurements, then problems of an inconsistency between the temperature dependence of P_s and $C-C_G$ occur, as well as inconsistencies between calculated and measured values of the change of transition temperature with applied electric field. Even ignoring these two points, in the region above $T/T_c=0.996$ the polarization drops faster than the calculation, as demanded by the heat capacity, and in accord with the known relationship between mean-field theory and experimental behavior near phase transitions. If we are correct in ignoring the two highest temperature points of Hill and Ichiki, we can then deduce that in the first-order transition in their sample the spontaneous polarization jumps to about 75% of its final value at T_c. We can use this value in the analog of the Clapeyron equation for ferroelectrics,

$$dT/dE=V\Delta P/\Delta S,$$

where dT/dE is the change of critical temperature with applied field, V is the molar volume, and ΔP and ΔS are the respective changes in spontaneous polarization and entropy at T_c, to find that $dT/dE=1.3\times10^{-4}$ °K cm/V. This value is to be compared with the experimental value deduced by Hill and Ichiki of $(1.9\pm0.3)\times10^{-4}$ °K cm/V. This may be taken to be at least acceptable agreement when it is realized that the measurements of Hill and Ichiki refer to a crystal of lower deuteration level (the transition temperature for their crystal was 215.75°K) which would be expected to have a smaller latent heat than the crystal on which the current measurements were made. In the above estimate we used the value of ΔS obtained from our work rather than the (presumably) smaller value appropriate for use in Clayperon's equation when applied to the sample employed by Hill and Ickiki. It is an open point at present if ΔS changes sufficiently rapidly with deuteration to resolve this possible discrepancy.



(a)

(b)

FIG. 5. Tests of the critical-point behavior of the heat capacity below T_c. (a) shows an attempt to fit the data to a power-law divergence of the form $1/(T_c-T^{1/2})$ which is the best power-law fit to the similar data for KDP and is the form predicted by the Ornstein-Zernike approximation and the form predicted above T_c by the exact theories of the two-dimensional KDP problem; (b) shows an attempt to fit the same data with a logarithmic divergence. The solid line represents

$$C-C_G=[-70\log_{10}(T_c-T)+64]\text{J/mole °K}. \qquad (T_c-T \text{ in °K}).$$

In assessing these two attempts to fit the critical-point behavior one might keep in mind that a mean-field theory can account for the data further than 1° from the transition.

Now let us turn our attention to an investigation of phenomena in the neighborhood of T_c. Since the transition is of first order, we expect, and find, a smaller contribution to the heat capacity from correlation phenomena than in KDP. We shall concentrate our attention on the data below T_c because it is only for these data that the role of C_G is relatively small and it is in this region that we have the best quality data. The two standard methods of the analysis of critical point heat capacities are presented in Fig. 5. Figure 5(a) presents a log-log plot of $C-C_G$ versus T_c-T in an attempt to fit the divergence to a power law. The solid line is a fit to a divergence of the form $1/(T_c-T)^{1/2}$ which is the power law which has been found to best describe KDP.[4,19] The fit to this divergence in the present case occurs over a somewhat smaller range in T_c-T than for KDP and shows similar evidence of an

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[18] B. Zwicker and P. Scherrer, Helv. Phys. Acta **17**, 346 (1944).

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"unhappy force fit" and rather severe "rounding" of the transition. This type of divergence is the sort predicted by the classical Ornstein-Zernike approximation[20] and also the type of divergence predicted *above* T_c by the exact solution to the two-dimensional analog of the KDP problem.[21] In Fig. 5(b) we plot C_G versus $\log_{10}(T_c-T)$ and attempt to fit the data to a logarithmic divergence. If anything, as in the case of KDP, the logarithmic divergence appears to be a slightly better fit than the power-law divergence, although the lack of sufficient data in the range $T_c-T<0.1°$ makes the analysis questionable. The preference for the logarithmic fit is perhaps made a bit stronger when we recall that the region of this fit, $T>219°\text{K}$, is precisely the region in which the data deviate strongly from the mean-field theory.

In conclusion, then, we find the transition to be of first order. We find that the SUS theory can give a reasonable account of the thermodynamic properties of DKDP in the region more than about 1°K away from T_c if we use the parameters $\epsilon_0/k=94.3°\text{K}$, $\epsilon_1/k=900°\text{K}$, and $\beta/k=35.6°\text{K}$. While an apparently reasonable set of parameters for describing the disordering contribution of the heat capacity of KDP can be obtained by scaling these parameters for the purpose of deducing the lattice-heat capacity, it is pointed out that these scaled parameters lead to contradictions with experiment in the case of KDP, so that more elaborate theories of the tunneling type are probably needed for a complete description of KDP. Finally, it is pointed out that the critical region in DKDP probably lies between 219°K and T_c and the divergence of the heat capacity is best described by a logarithmic divergence in this region.

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Crystal Dynamics and Magnetic Excitations in Cobaltous Oxide

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The low-lying phonon and magnetic excitations of CoO have been studied experimentally and theoretically, both above and below the antiferromagnetic ordering temperature. The experiments were performed using the technique of inelastic scattering of slow neutrons with the aid of a triple-axis crystal spectrometer. These experiments were difficult because the phonon and magnetic excitations have very similar frequencies, and also because the specimen has a domain structure in the antiferromagnetic phase. Nevertheless, models were obtained for the phonon spectra. The magnetic spectra of the paramagnetic phase can be understood if the spin-orbit coupling parameter of Co^{2+} of CoO is reduced to 40% of its free-ion value. With this value it is then possible to understand the excitations in the antiferromagnetic phase in at least a qualitative way by introducing nearest- and next-nearest-neighbor exchange parameters. A detailed evaluation of this theory of the magnetic excitations is not possible, because of the difficulties encountered in the experimental part of the study; nevertheless, it is believed that the description given here is essentially correct.

I. INTRODUCTION

The magnetic properties of cobaltous oxide (CoO) are of considerable interest both theoretically and experimentally. Experimentally it is of interest that CoO is an antiferromagnet with a high Néel temperature, about 293°K, and in its paramagnetic phase it has the cubic NaCl structure. From the theoretical aspect CoO is of interest because the Co^{2+} ion has orbital angular momentum which is not quenched entirely by the cubic crystalline field. There are some low-lying excited states of the Co^{2+} ion, and it is of interest to determine the extent to which they modify the magnetic properties.

In its antiferromagnetic phase, CoO has a tetragonal crystal structure in which the atomic magnetic moments are arranged in ferromagnetic sheets in (111) crystallographic planes.[1–3] There is some doubt[3] concerning the actual alignment of the moments in each plane, because the data obtained from neutron-diffraction experiments on single-crystal specimens may be interpreted in terms of either the collinear spin model of Roth[1] or by the multispin axis model of van Laar.[2] At present, the weight of evidence favors the collinear spin model, particularly in view of the recent experiments by Saito *et al.*[4] Measurements have been made of the

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