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Thermodynamic Properties of KH_2AsO_4 and KD_2AsO_4

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Measurements of the specific heat and electric susceptibility of KH_2AsO_4 and KD_2AsO_4 have been performed in the region of their respective ferroelectric transitions. Both substances undergo first-order transitions with latent heat of 300 and 570 J/mole, respectively. The entropy associated with the transition is found to be $0.506R$ and $0.500R$, respectively. The Curie constants are found to be 187 and 358 K, respectively. The thermal data are used to deduce the spontaneous polarization. The polarization thus deduced agrees with electrocaloric data for KH_2AsO_4, the only case where independent polarization data are available. The maximum spontaneous polarizations are found to be 5.25 and 7.20 $\mu C/cm^2$, respectively. It is shown that the theory of Silsbee, Uehling, and Schmidt provides an excellent description of the thermodynamic properties of both materials.

I. INTRODUCTION

Potassium dihydrogen phosphate (KDP) and its deuterated isomorph (KD*P) are the primal members of a class of order-disorder ferroelectrics[1] whose behavior has been explained in terms of the ordering of protons in double-minimum hydrogen bonds.[2] Although a complete description of the ferroelectric behavior requires a discussion of the coupling of the protonic motion to the lattice modes,[3] statistical theories which are elaborations of the basic Slater model are widely used in the discussion of KDP. The most comprehensive such theory is that developed by Silsbee, Uehling, and Schmidt[4] (SUS) which has been used in the discussion of the static[5] and dynamic[6] properties of KDP and KD*P. One result of comparisons of the SUS theory with experiment is the finding that the theory better describes KD*P than it does KDP. This is taken to indicate that tunneling plays a significant role in KDP but not in KD*P. Extensions of the SUS model which incorporate tunneling[7] allow a satisfactory description of the thermodynamic properties of KDP.

This paper reports an investigation of the arsenate analogs of KDP and KD*P (KDA and KD*A, respectively) in which a number of thermodynamic properties relating to the ferroelectric transition have been determined and compared with the SUS theory. The basic measurements which have been performed are calorimetric: Specific-heat and latent-heat data are reported. In addition, dielectric-constant data are reported for KD*A, since such data are otherwise unavailable. Polarization data are deduced from the calorimetric data through use of the thermodynamic theory of ferroelectrics[8] which, in the case of KDA, agrees with electrocaloric determinations of the polarization.[9] The SUS theory is shown to provide an excellent description of both KDA and KD*A, implying that tunneling plays an insignificant role in either material. In addition to the thermodynamic data, the results of dielectric relaxation in the paraelectric phase of KDA are reported.

II. APPARATUS

The experiments were performed in a vacuum adiabatic calorimeter previously described by Reese and May.[10] The sample is suspended in a heated can whose temperature is maintained at the sample temperature. Temperature errors are sensed by a differential thermocouple which generates the input to the circuit controlling the heat input to the can. The control circuit operates simultaneously in the proportional and reset modes.

The temperature sensors were low-temperature thermistors (Keystone-type RL10X04), the resistance of which was determined using a 37-Hz low-power Wheatstone bridge. The thermistors were calibrated against a Pt resistance thermometer which had been calibrated by the National Bureau of Standards. Calibration data were obtained between 90 and 200 K by mounting the thermistors and the Pt thermometer in intimate thermal contact with each other inside the calorimeter used for the main body of the experiments. The values of (R, T) were locally fit to a second-order expansion of the form

$$\ln R = \ln R_\infty + a/T - b/2T^2$$

or

$$\ln R = \ln R_0 - aT + \tfrac{1}{2}bT^2 .$$

The form which gave the smallest deviation from the data in any particular temperature range was employed. Over a temperature range of 10 K the deviation of a given fit from the calibration data was less than 15 mK. In the work on KD*A a more extensive temperature range was investigated requiring a different fit approximately every 10-K interval.

III. SPECIFIC HEAT

Specific-heat data for KDA over a wide range of temperatures have been previously reported.[11] Since these results were obtained using a powdered sample, it was decided to reinvestigate a limited temperature region in the vicinity of the transition temperature. This decision was made since past experience with KDP has shown that near T_c the data from powdered samples can be misleading. For KD*A there are no available heat-capacity data, so a much broader temperature range was investigated.

Single-crystal samples were employed for all measurements reported here. Two KDA samples were obtained from Gould Laboratories[12] with nominal dimensions $\frac{1}{2}\times\frac{1}{2}\times\frac{1}{4}$ in. and masses of approximately 3.1 g. The KD*A sample was obtained from Quantum Technology Ltd.[13] and had a mass of 4.39 g. The samples were prepared for specific-heat and dielectric-constant measurements by depositing 500-Å evaporated gold electrodes on the z faces. The thermistor was wrapped in a copper foil, one part of which was soldered to one lead of the thermistor. The copper foil terminated in a flag with an area of approximately 0.5 cm^2 which was attached to one side of the sample with GE 7031 varnish. The purpose of this foil configuration is to promote thermal contact between the thermometer and the sample. Previous experience has shown this to be a necessary precaution. A heater consisting of a length of 0.002-in.-diam maganin wire with a total resistance of 100 Ω was wrapped about the sides of the crystal and held in place with varnish. The sample was then mounted by nylon threads.

The heat-capacity contribution of the addenda for the KDA experiment was determined by comparison with the results of Stephenson and Zettlemoyer[11] by matching our heat-capacity results to theirs at the extremes of the range covered by our measurements. The addenda contribution for the KD*A experiment was estimated on the basis of previous measurements in this laboratory of addenda of similar composition. The contribution to the total heat capacity by the addenda amounted at most to 14% and 6% for KDA and KD*A, respectively. In the region where there is a substantial contribution to the heat capacity due to the ferroelectric transition the addenda contribution was a much smaller percentage of the total.

The specific-heat data are shown in Figs. 1 and 2. These data indicate transitions at $T_c = 96.15$ and 161.02 K for KDA and KD*A, respectively. The observed transitions were of first order with the bulk of the entropy change occurring at T_c. In KDA the typical signatures of a first-order transition, isothermal absorption of heat, superheating, and supercooling were all observed. It was observed that KD*A could be superheated or supercooled, but the transition was broadened over an interval of approximately 300 mK when observed by discontinuous heating. This likely reflects a distribution of transition temperatures over the crystal caused by an inhomogeneous deuteron distribution. The latent heats deduced were (300 ± 1) and (570 ± 5) J/mole for KDA and KD*A, respectively. The errors do not take into account any problems in exactly locating the transition. For KD*A a correction to the measured transition enthalpy has been made to take account of heat supplied over the 300-

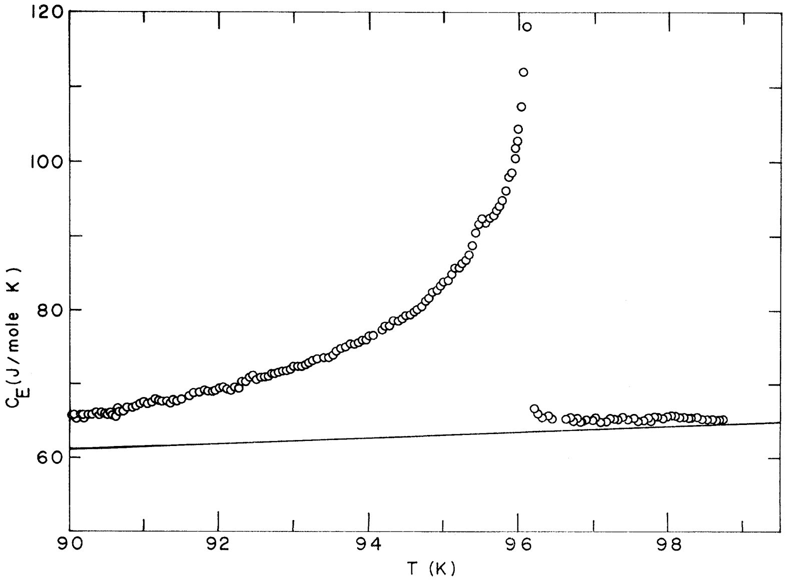

FIG. 1. Total specific heat C_E vs temperature for KH_2AsO_4. The solid line represents the lattice contribution to the specific heat C_p.

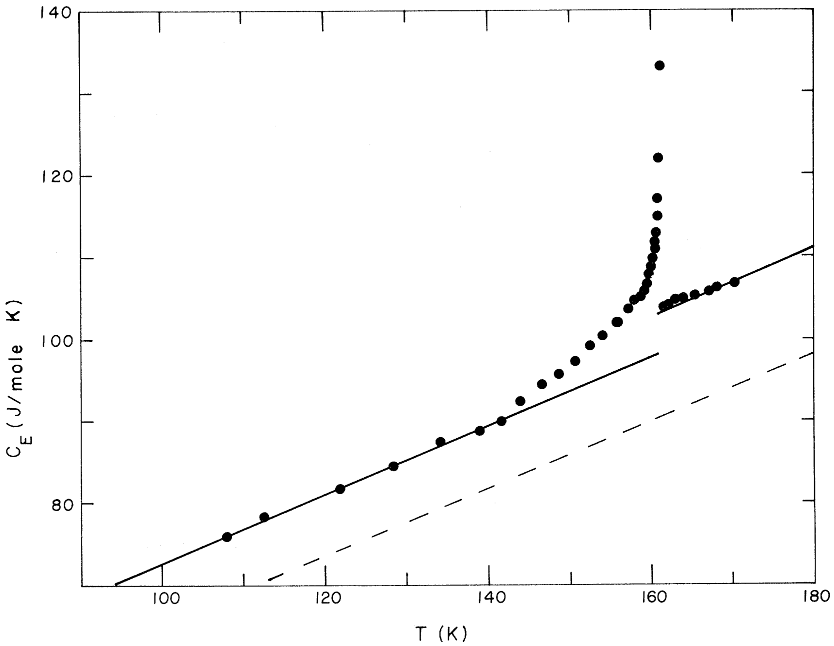

FIG. 2. Total specific heat C_E vs temperature for KD_2AsO_4. The solid line represents the lattice contribution to the specific heat C_p for KD_2AsO_4, the dashed line is C_p for KH_2AsO_4.

mK interval which was not directly utilized for the destruction of the ferroelectric state.

In order to adapt specific-heat data to the discussion of the ferroelectric transition it is necessary to effect a separation of the measured heat capacity (C_E) into two parts: a part associated with the temperature dependence of the polarization (ΔC) and the remainder (C_P). Above T_c, C_P equals the heat capacity measured in this experiment, $C_{E=0}$. A variety of techniques may be employed for this separation below T_c, the simplest of which is to make a "reasonable" estimate of C_P. For KD*A this is not too difficult since the data show a weak temperature dependence except in the immediate vicinity of T_c. Thus, it is natural to extrapolate the data below about 140 K upwards as an estimate of C_P. This resulting curve is roughly parallel to the heat-capacity curve of KDA in this temperature region. The resultant estimate of C_P is shown in Fig. 2 by the solid line. For KDA the ferroelectric transition is slightly less abrupt than in KD*A and occurs at lower temperatures where the temperature dependence of C_P is greater than is the case near the transition in KD*A. Thus, there are more problems in establishing a reliable estimate of C_P. This estimate was established by performing an extrapolation of the low-temperature data of Stephenson and Zettlemoyer. The resulting estimate is depicted by the solid line in Fig. 1.

The estimate of C_P for KD*A shows an apparent discontinuity of approximately $0.6R$ at T_c. Such a feature is in accord with the predictions of theories of the SUS type and results from thermal excitation of higher-energy proton configurations. No similar feature is apparent in C_P as deduced for KDA. Whether this is a result of the greater uncertainties involved in the deduction of C_P for KDA than for KD*A or its actual absence is open to question. One must keep in mind that there are changes in the lattice structure which take place at T_c and that these may cause changes equal to or larger than those resulting from the thermal excitation of higher-energy proton configurations. For example, evidence derived from electrocaloric studies of KDP indicates that C_P is approximately R *lower* above T_c than it is below T_c.[14]

Using the indicated decomposition of the heat capacity, one finds the portion directly associated with the ferroelectricity ΔC as given in Figs. 3 and 4. This can be discussed in terms of the entropy recovered at a temperature T,

$$\Delta S_t(T) = \Delta S_0 + \Delta S(T),$$

where

$$\Delta S_0 = L/T_c$$

and

$$\Delta S(T) = \int_T^{T_c} (\Delta C/T)\, dT.$$

Here L is the latent heat. The entropy change at T_c and the total entropy change associated with the transition are given in Table I. For both compounds the total entropy associated with the transition is approximately $0.5R$, slightly larger than in either KDP or KD*P. Unlike the case of KDP, there is no isotope effect on the entropy.

According to the thermodynamic theory of ferroelectricity[8] the recovered entropy can be related to the polarization according to

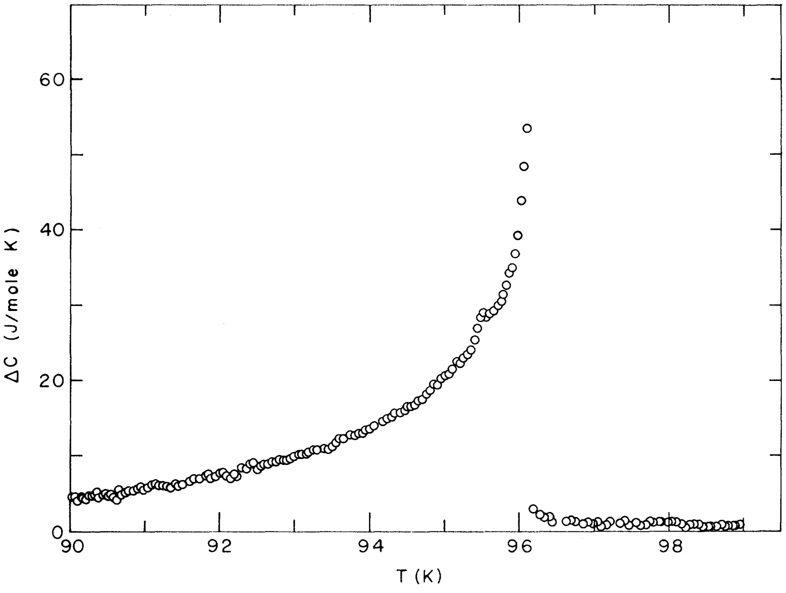

FIG. 3. Difference between the total specific heat and the lattice specific heat C_E-C_p vs temperature for KH_2AsO_4.

$$P^2(T) = (2/V_0\alpha)\Delta S_t(T),$$

where V_0 is the molar volume and $1/\alpha$ is the Curie constant. The maximum saturation polarization $P(0)$ and the polarization jump P_0 at T_c for both materials are included in Table I. The maximum saturation polarization is considerably affected by isotopic substitution. Plots of the spontaneous polarization as functions of temperature in reduced variables are given for both compounds in Fig. 5.

The use of the thermodynamic theory to relate calorimetric and polarization data has been extensively verified, even quite close to T_c, by Benepe and Reese[14] for KDP, a similar material. Further justification of our analysis is indicated since the polarization deduced for KDA fits the polarization measurements of Wiseman,[9] if one includes the portion termed by Wiseman "relaxation polariza-

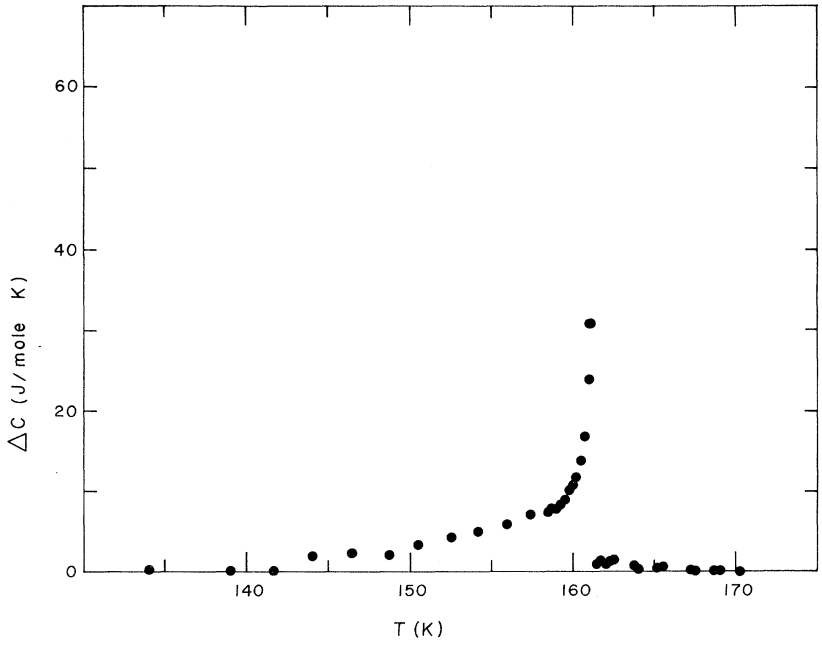

FIG. 4. Difference between the total specific heat and the lattice specific heat C_E-C_p vs temperature for KD_2AsO_4.

TABLE I. Thermodynamic properties of KDA and KD*A and their comparison with the predictions of SUS theory.

Property	KDA experiment	SUS	KD*A experiment	SUS
L/RT_c	0.377	0.376	0.426	0.409
$\Delta S(0)/R$	0.129	0.165	0.074	0.098
$\Delta S_t(0)/R$	0.506	0.541	0.500	0.507
$P_0/P(0)$	0.862	0.866	0.922	0.918
$P(0)$ ($\mu C/cm^2$)	5.25	···	7.20	···
$1/\alpha$ (K)	187	191	358	363
θ (K)	94.25	94.74	153.0	157.36
ϵ_0/kT_c	···	0.36	···	0.345
ϵ_1/kT_c	···	3.92	···	4.26
β/kT_c	···	0.2057	···	0.2078

tion." This is also indicated in Fig. 5.

IV. DIELECTRIC EFFECTS

In the paraelectric region the electric susceptibility was observed to obey the Curie-Weiss law $1/\chi = \alpha(T - \theta)$ except in the region close to the transition. This is illustrated for KD*A in Fig. 6. On the basis of electrocaloric-effect measurements Wiseman found $1/\alpha$ to be 187 K for KDA. Our data give the Curie constant as 182 K for KDA and 358 K for KD*A. This large isotope effect upon the Curie constant is in distinct contrast to the case of KDP in which substituting deuterons for protons causes almost no change in the Curie constant.

It was our intent to measure the spontaneous polarization using the electrocaloric effect. This involves applying an electric field and measuring the charge flow and temperature change. These experiments were not successful because the samples had a tendency to undergo dielectric breakdown at the electric fields required to produce single-domain configuration. In addition, the process was complicated by an extremely long relaxation effect (on the order of 1000 sec). The relaxation manifested itself as a gradual change in polarization after an initial change in electric field and was observed in both KDA and KD*A. Because of domain effects the relaxation was complicated below T_c. Above T_c it was approximately exponential with a relaxation time for KDA given by

$$\tau = 640/(T-T_c)^{1/2} \text{ sec } K^{1/2}.$$

Similar measurements were not obtained for KD*A.

The actual mechanism involved in this relaxation is not known. It appears many orders of magnitude

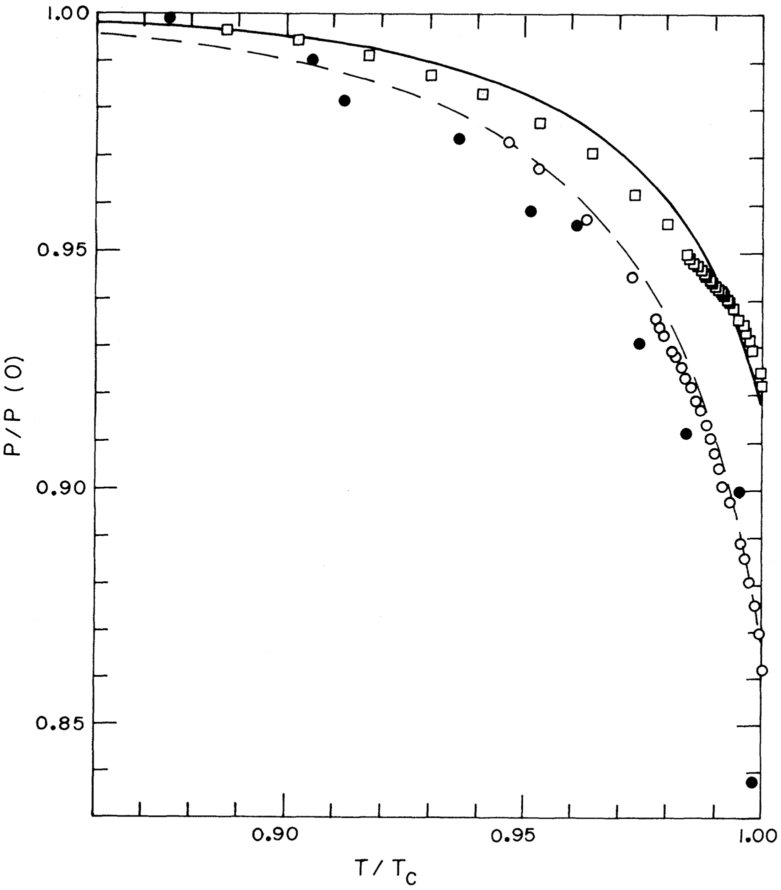

FIG. 5. Comparison of the spontaneous polarization divided by its value at 0 K, $P(0)$, for KH_2AsO_4 [open circles from specific heat, solid circles from electrocaloric measurements (Ref. 9), and dashed line from SUS fit] and KD_2AsO_4 (open squares from specific heat and solid line from SUS fit) vs reduced temperature.

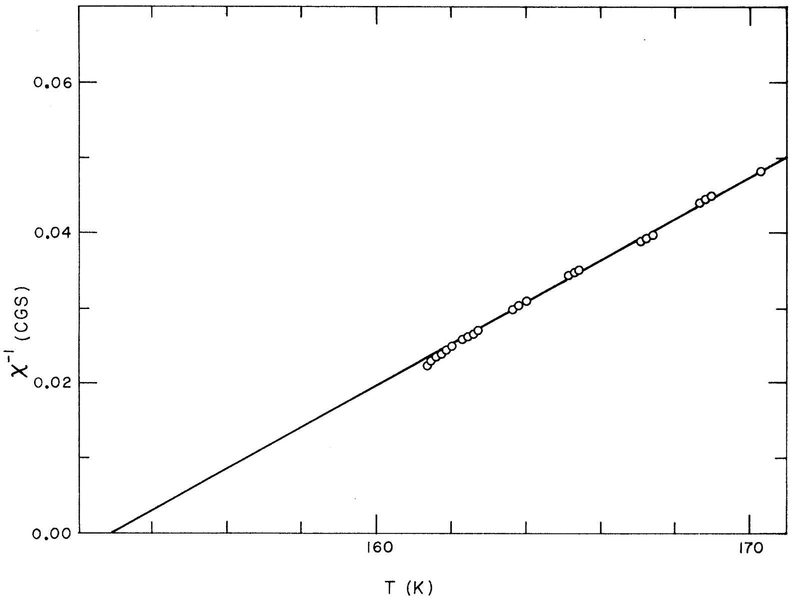

FIG. 6. Inverse electric susceptibility vs temperature for KD_2AsO_4 in the Curie-law region.

too fast to be associated with the measured conductivity of the crystals. There is a possibility that it may represent an anomalous charge flow on the sample surface and that it might be connected with the rather low breakdown fields observed. However, this is merely speculation. Similar slow relaxation has been reported for KDA by Blinc and Bjorkstam[15] in association with nuclear-magnetic-resonance experiments and by Wiseman[9] in electrocaloric measurements. Thus, such dielectric relaxation may be an inherent property of KDA and KD^*A. Within the context of the SUS theory the relaxation should be identified with the jump process for Takagi groups. However, in that case one would expect a stronger temperature dependence than was observed.

V. THEORY

The SUS theory is a statistical treatment of the possible configurations of protons (or deuterons) within double-minimum hydrogen bonds about a PO_4 group. Energies of zero and ϵ_0 are assigned to two types of H_2PO_4 configurations and an energy of ϵ_1 is assigned to HPO_4 and H_3PO_4 configurations. A mean-field coupling term of the form βP^2 is added to the Hamiltonian. Treating ϵ_0, ϵ_1, and β as adjustable parameters we have fit the SUS theory to the reduced polarization curves. A requirement of the fit was that the transition occurred at $T/T_c = 1$, so that for each curve there were two adjustable parameters. The results of the fitting procedure are shown in Fig. 5. The parameters used for the fit are given in Table I where the experimentally derived thermodynamic parameters of KDA and KD^*A are compared with the calculations. Since the SUS theory is consistent with the thermodynamic theory used to obtain the polarization from the specific heat, and since both the Curie constant and reduced polarization are correctly predicted, the theory will fit the heat capacity and latent heat.

The result of this comparison is the conclusion that SUS theory provides an excellent description of all the thermodynamic properties of KDA and KD^*A. This is in contrast to the case of KDP where the SUS theory predicts incorrect values for the entropy and Curie constant. Since the failure of SUS in this case is taken to indicate the role of tunneling in KDP, we may conclude that there is no evidence of tunneling in either KDA or KD^*A. However, one cannot conclude that all is satisfactorily understood since Blinc and Bjorkstam[15] have deduced a value for ϵ_0 for KDA using the SUS theory to analyze the results of nuclear-quadrupole-resonance experiments on As^{75}. Their value of $\epsilon_0/kT_c \approx 0.56$ is considerably different from the value needed to give a good account of the thermodynamic properties. This may indicate that the SUS model cannot simultaneously describe both the static and dynamic properties of KDA.

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Heat Capacity of Hexagonal NiS: Metal-Nonmetal Transition[*]

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The heat capacity of hexagonal NiS has been measured from 35 to 330 °K. Changes in enthalpy and entropy across the metal-nonmetal transition were found to be 1383 J/mole and 5.03 J/mole deg, respectively. Measurements near the critical temperature have been made in extreme detail.

I. INTRODUCTION

A large amount of interest has recently been shown in trying to explain the metal-nonmetal (MNM) phase transition which occurs in some solids. Although this type of transition was originally proposed by Mott in 1949,[1] there are experimental and theoretical reasons for a revival of work directed toward explaining the phenomena. Experimental advances in material preparation have led to new measurements on relatively pure samples and it has been found that quite a large number of compounds exhibit the MNM transition. It is now known that the MNM transition should not be considered a rare and exceptional case, but rather a frequently observed phenomenon which demands an adequate explanation. Theoretically, the MNM transition remains a challenging and largely unsolved problem. One-electron theory is simply inadequate to explain it, and the transition is one of the more striking many-body effects in solid-state physics. At present the many-body theory of this transition is highly speculative at best and consists largely of proposed "mechanisms" which drive the transition rather than fundamental calculations.

Of critical importance to a theory of the MNM transition is the manner in which it predicts the thermodynamic behavior of a solid at this transition. That is, is the transition of first or second order, what is the entropy and enthalpy change at the transition, and what is the temperature dependence of the thermodynamic functions near the transition? This paper reports the results of measurements of the specific heat near the MNM transition in NiS. In addition, values of the entropy and enthalpy changes at the transition are given and some comments are made about the thermodynamic order of the transition.

Stoichiometric NiS crystallizes in two structures, a rhombohedral phase (millerite)[2] and a hexagonal phase (NiAs).[3] Although the rhombohedral phase is the stable phase at room temperature, the hexagonal phase can be made to exist stably at room temperature by quenching it from above 652 °K. This hexagonal phase exhibits a sharp MNM transition near 270 °K.[4] In addition, neutron diffraction studies have shown that the material becomes antiferromagnetically ordered at this same temperature.[5] Below the transition temperature, the magnetic structure is found to be a simple two-sublattice structure in which the magnetic moments of the Ni atoms are coupled ferromagnetically within $\{001\}$ planes and antiferromagnetically between adjacent $\{001\}$ planes. This results in the magnetic unit cell being identical to the chemical unit cell. Furthermore, it is found that the sublattice magnetization is within 10% of saturation upon ordering. There is apparently little or no magnetic moment associated with the Ni atoms above the transition in the metallic state.

In addition to the powder neutron diffraction