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Low-Temperature Magnetic and Thermal Properties of $NiSnCl_6 \cdot 6H_2O$[†]

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$NiSnCl_6 \cdot 6H_2O$ forms rhombohedral (trigonal) crystals containing one axially distorted octahedral $[Ni(H_2O)_6]^{++}$ complex per unit cell. Measurements of (a) the magnetic susceptibility, (b) isothermal magnetization, and (c) magnetic heat capacity between ~ 0.35 and 4.2 K can be described by the spin Hamiltonian $\mathcal{H}=DS_z^2+g\mu_B\vec{S}\cdot\vec{H}$ for $S=1$ with $D/k=+0.64$ K and $g=2.25$. The ground-state triplet is thus split in zero field into a lower singlet and an upper doublet. There is also evidence of antiferromagnetic coupling among Ni^{++} ions which is weak in comparison with this splitting. A system of this type should exhibit unusual properties for $T<D/k$. Exploratory magnetocaloric observations with $H \parallel$ trigonal axis reveal cooling by adiabatic magnetization for $H \le D/g\mu_B$. They also suggest the establishment of spin order at sufficiently low temperatures for $H \sim D/g\mu_B$.

INTRODUCTION

It was pointed out[1,2] a number of years ago that a system of weakly interacting ions or molecules with a nondegenerate ground state separated by $\Delta \sim 1-10$ cm^{-1} from a degenerate excited state should cool upon adiabatic magnetization if the initial temperature $T_i \ll \Delta/k$. Such cooling has been realized experimentally[3,4] in $Cu(NO_3)_2 \cdot 2.5H_2O$. This is a system in which Cu^{++} ions ($S=\frac{1}{2}$) are predominantly coupled in pairs by isotropic antiferromagnetic exchange interaction such that $\Delta = J = 5.2k$, the excited state of interest being a spin triplet. Another kind of salt which might be expected[2] to show this effect would be one containing the Ni^{++} ion in an axially distorted octahedral crystalline field. The ground state of such an ion consists of a spin triplet ($S=1$) whose splittings are described by a spin Hamiltonian[5]

$$\mathcal{H}=DS_z^2+g\mu_B\vec{S}\cdot\vec{H} , \tag{1}$$

where g is usually isotropic as indicated. For $D>0$ and $H=0$, the triplet is split into a lower singlet separated by an energy D from an excited doublet. For $D<0$, the doublet lies lowest.

The energy eigenvalues of Eq. (1) with the field applied parallel and perpendicular to the axis of the distortion (z axis) are, respectively,

$$W_\parallel = 0, \quad D \pm g\mu_B H_\parallel \tag{2}$$

$$W_\perp = D, \quad \tfrac{1}{2}D \pm [(D/2)^2+(g\mu_B H_\perp)^2]^{1/2} . \tag{3}$$

In Fig. 1 the effect of magnetic fields applied parallel and perpendicular to the z axis is shown for the case $D>0$. For $T_i \ll D/k$, adiabatic increase of $H(\lesssim D/g\mu_B) \parallel z$ causes the lower component of the doublet to approach the stationary singlet without appreciable change in their populations. Thus the temperature of the spin system falls and with it the temperature of the crystal lattice whose heat capacity would usually be very small near $T_i \sim 1$K. When H exceeds $D/g\mu_B$, the two lower levels diverge and further increase in H produces the conventional paramagnetic heating. Note that for $H \perp z$ the levels always diverge and no cooling will accompany adiabatic magnetization.

In practice the sharp level crossing shown in Fig. 1(a), and the degeneracy which it implies, will not occur. A number of mechanisms can cause these levels to mix and repel one another. These include[2] misalignment of the field and the z axis of the octahedral complex, further distortions of the crystal field, and interactions among the Ni^{++} ions. The minimum energy separation of the two levels allowed by the dominant mechanism imposes a lower limit on the temperature attainable in the adiabatic magnetization process.

A much simpler practical limitation has, until now, made it impossible to observe magnetic cool-

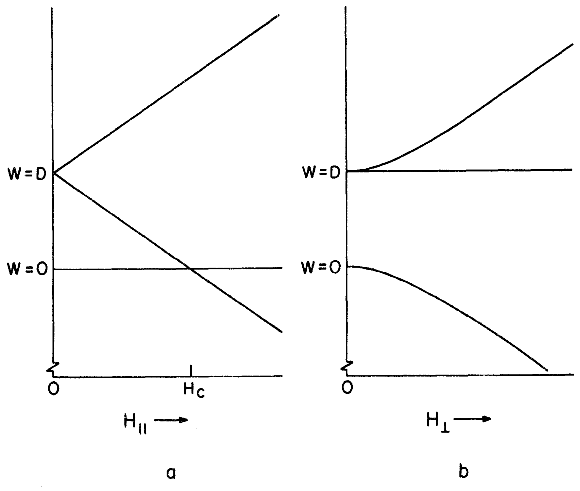

FIG. 1. Schematic diagram of field dependence of eigenvalues of the spin Hamiltonian $\mathcal{H}=DS_z^2+g\mu_B\vec{S}\cdot\vec{H}$ for $S=1$ and $D>0$. (a) $H \parallel$ trigonal axis; (b) $H\perp$ trigonal axis.

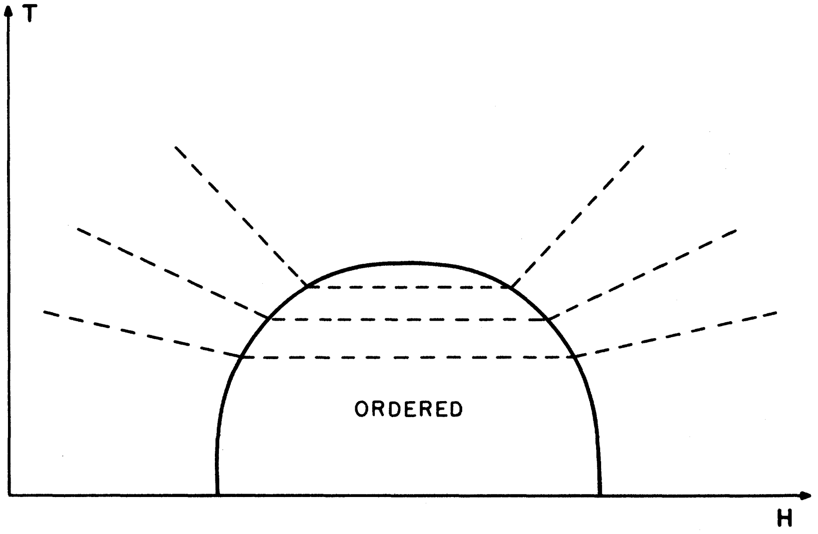

FIG. 2. Schematic H, T phase diagram of system whose single-ion ground state is as in Fig. 1(a) but with subcritical spin coupling. In molecular field approximation solid curve is line of second-order transition points and isentropic lines are as shown by dashed curves (after Refs. 8 and 9).

ing of this type in concentrated salts containing Ni^{++} or, to our knowledge, any other ion with a similar ground state, e.g., V^{+++}. Those salts in which it has been found[6] that $D > 0$ are, unfortunately, also those whose unit cells contain more than one Ni^{++} ion. These and their surrounding ligands are so arranged that the local z axes are not parallel. Thus it has not been possible to have $H \parallel z$ at all ions simultaneously and the cooling of one group is partially or fully nullified by the heating of the other ions.

We have felt it to be a matter of some interest to find a salt containing a single axially distorted octahedral Ni^{++} complex per unit cell with $D > 0$. One of our motives was, of course, the desire to observe cooling by adiabatic magnetization as outlined above. We were equally intrigued, however, by another possibility which access to such a salt might open up to us. Ironically, this possibility arises for a reason which limits the cooling effect, namely, the presence of significant interaction among Ni^{++} ions.

It was shown by Moriya[7] that if the triplet ground state of the Ni^{++} ion is split so as to leave a singlet lowest ($D > 0$) and if the interaction energy is less than a certain fraction of the splitting then, at least in a molecular field approximation, no cooperative magnetic ordering can occur at any temperature. Moriya's prediction assumes that no magnetic field is applied to the system. The situation is different if each ion experiences $H \parallel z$ such that $H \sim D/g\mu_B$. At a sufficiently low temperature the (near) degeneracy produced in the single ion can be lifted by cooperative interaction and long-range order of an unusual type[8,9] can be established among the field-induced moments. Note that this possibility exists only for H within a certain range above and below $D/g\mu_B$ so that the ordered phase occupies the limited portion of the H-T diagram shown in Fig. 2. This type of phase diagram is very different from those of conventional antiferromagnets or metamagnets. Recent evidence[10] suggests that $Cu(NO_3)_2 \cdot 2.5H_2O$ possesses such a phase diagram. We have been curious to see whether a nickel salt could be found which would order in this fashion.

Several nickel salts in which interactions among Ni^{++} ions are "subcritical," in the sense that they cannot produce long-range order at any temperature in the absence of an applied field, have been identified.[6,11] Unfortunately, all of them contain ions which are inequivalent for the present purpose and in some cases, although $D > 0$, rhombic crystal field components cause the ground-state triplet to be fully split in zero field. It becomes desirable, therefore, to look for other likely materials.

A compound with one $[Ni(H_2O)_6]^{++}$ complex per unit cell is $NiSiF_6 \cdot 6H_2O$.[12] Paramagnetic-resonance studies[13] have established that the departure of the crystal field from octahedral symmetry is purely axial (trigonal) and that $|D|$ increases rapidly with T. Magneto-optical measurements[14] indicate that $D < 0$. By compressing crystals of this salt hydrostatically at room temperature, however, Walsh[15] has been able to change the sign of D. $NiSiF_6 \cdot 6H_2O$ belongs to a family of isostructural trigonal (rhombohedral) crystals[12,16] which includes several other salts of Ni^{++} for which only very limited susceptibility data and no resonance results are available. Because of the evident sensitivity of D in the fluosilicate to unit-cell shape through deformation and thermal expansion, we decided to examine at least one of these related compounds, namely, $NiSnCl_6 \cdot 6H_2O$, the structural prototype.[12] As we shall see, this salt seems to possess several of the desired properties.

Nickel chlorostannate hexahydrate forms trigonal (rhombohedral) crystals belonging[12] to the space group $R\bar{3}$. The unit cell is unimolecular with parameters $a_0 = 7.09$ Å and $\alpha = 96°45'$ as compared with $a_0 = 6.255$ Å and $\alpha = 96°6'$ for $NiSiF_6 \cdot 6H_2O$. The $[Ni(H_2O)_6]^{++}$ complex forms a nearly regular octahedron ($Ni^{++} - H_2O$ separation ~ 2.4 Å) and is located at the center of the unit cell. This complex is trigonally distorted along the trigonal axis of the crystal (c axis). The eight corners of the unit cell are occupied by $SnCl_6^{--}$ octahedra. Apart from the structural data, the only other relevant information available prior to the present work consisted of measurements[17] of magnetic anisotropy ($\chi_{\parallel} - \chi_{\perp}$) and of $\chi_{\perp}$ between 90 and 300 K. These results suggest that, at these temperatures at least, $D < 0$. However, this conclusion is not supported by our own observation at low temperatures or recent paramagnetic-resonance studies[18] between 1.4 and 370 K.

In the work to be described, we have employed several different techniques to study the nature of the ground state of the Ni^{++} ion in $NiSnCl_6 \cdot 6H_2O$ and possible interaction among such ions. These are measurements of (a) powder and single-crystal magnetic susceptibilities between 0.35 and 4.2 K; (b) magnetization between 1.35 and 4.2 K with 40 kOe $> H \parallel z$; and (c) heat capacity of powder and single-crystal specimens between 0.35 and 4.2 K. In addition, we have performed some exploratory magnetocaloric measurements on a single-crystal specimen at temperatures below ~ 0.5 K. In the next section, some details of the experimental methods are outlined. The results and their interpretations are presented in the final section of the paper.

EXPERIMENTS

The specimens employed in this work were prepared by slow evaporation at 30 °C < T < 40 °C of an equimolar aqueous solution of $NiCl_2$ and $SnCl_4$. The starting materials were either Baker Analyzed Reagent Grade or Fisher Certified Reagent Grade $NiCl_2 \cdot 6H_2O$ and Baker Analyzed Reagent Grade $SnCl_4 \cdot 5H_2O$. Clear medium-dark green crystals of $NiSnCl_6 \cdot 6H_2O$ were obtained. The trigonal axis (c axis) was easily identified by inspection.

Magnetic susceptibilities of powder and single-crystal specimens were measured by an audio-frequency mutual-inductance technique between 0.35 and 4.2 K in a He^3-cooled cryostat which has been previously described.[19] The data reported here were taken at 275 Hz.

We have measured magnetization isotherms at temperatures between 1.35 and 4.2 K in fields up to 40 kOe applied along the trigonal axis of a rodlike specimen. The specimen was essentially moved out of a coil fixed in the uniform field at the center of a small superconducting solenoid and the induced signal measured by a ballistic galvanometer. Details of the technique have been given elsewhere.[20]

Heat-capacity measurements were performed in a He^3-cooled vacuum calorimeter[21,22] which could be placed in the gap of a c-type electromagnet giving fields up to ~ 10 kOe for magnetocaloric observations. Powder samples were held, together with a small amount of He^3 gas, in a copper capsule which was cooled by means of a mechanical heat switch. A germanium resistance thermometer attached to this capsule was calibrated against the vapor pressures[23,24] of He^3 and He^4 at numerous points in the interval 0.37–4.2 K. We estimate the accuracy of the temperature scale thus established to be ± 0.010 K for $T < 0.5$ K and ± 0.005 K for $T > 0.5$ K. The heat capacity of the capsule was determined in a separate series of experiments.

Single-crystal specimens were attached with GE 7031 lacquer to a small copper holder which was slotted to minimize eddy-current heating. The exposed crystal faces were coated lightly with vacuum grease. A 1/10-W, 27-Ω Allen–Bradley carbon resistor was also lacquered into a hole in the specimen holder to serve as a thermometer. The mechanical heat switch could not be used to cool this specimen and its holder. This was accomplished with helium gas. The trigonal axis of the specimen crystal was aligned with an applied field to within ± 2°. Since direct calibration of the carbon thermometer against the vapor pressure of liquid He^3 or He^4 was possible only above ~ 0.52 K, it was necessary to extrapolate the R-T relation in some cases down to ~ 0.3 K. This was done using the approximate linear dependence[25] of $\log T$ on $\log[-(1/R)(dR/dT)]$ observed above 0.52 K. Where necessary, corrections for the magnetoresistive effect[26] in the carbon thermometer were also applied. The heat capacity of the holder was no more than 10% that of the specimen crystal between ~ 0.3 and 1 K.

RESULTS AND DISCUSSION

Magnetic Susceptibility

Values of the magnetic susceptibilities of powdered and single-crystal specimens of $NiSnCl_6 \cdot 6H_2O$ between 0.35 and 4.2 K are shown in Fig. 3. These results are representative of several different experimental runs. The single-crystal data were taken with the small oscillatory measuring field parallel and perpendicular to the trigonal axis. There was no suggestion of anisotropy in $\chi_{\perp}$.

The fact that $\chi_{\perp} > \chi_{\parallel}$ in Fig. 3 immediately indicates that $D > 0$ in this salt at these temperatures and that the ground-state triplet is split into a lower singlet and an upper doublet. This becomes clear when one writes the expressions for $\chi_{\parallel}$ and $\chi_{\perp}$ calculated with the field-dependent eigenvalues of the spin Hamiltonian, Eq. (1), namely, Eqs. (2) and (3). These are

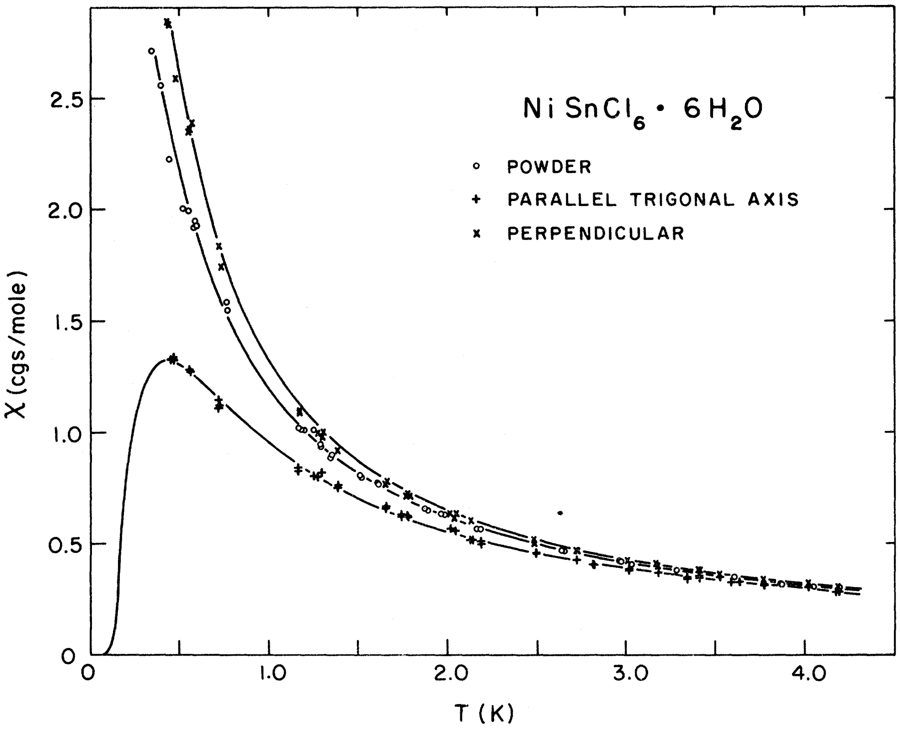

FIG. 3. Magnetic susceptibilities of powder and single-crystal specimens of $NiSnCl_6 \cdot 6H_2O$. Solid curves are calculated with $g = 2.25$, $D/k = +0.64$ K, and $n = -0.02$ mole/emu.

$$\chi_{\parallel}^0 = \frac{2N_0 g^2 \mu_B^2}{kT}\,\frac{1}{e^{D/kT}+2}\;, \tag{4}$$

$$\chi_{\perp}^0 = \frac{2N_0 g^2 \mu_B^2}{D}\left(\frac{e^{D/kT}-1}{e^{D/kT}+2}\right)\;. \tag{5}$$

For $D > 0$, we see from these equations that $\chi_{\perp}^0/\chi_{\parallel}^0 = (kT/D)(e^{D/kT} - 1) \gtrsim 1$ at all temperatures. Equations (4) and (5) have been fitted to all the data of Fig. 3 assuming $\chi_p = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$ and using a least-squares procedure to optimize the choice of parameters g and D. The best fit was given by $g = 2.20$ and $D/k = +0.65$ K.

An improvement in the fit of the susceptibility data was obtained by supposing that the Ni^{++} ions in this salt interact and that this interaction can be treated in a simplified molecular field approximation. Formally this amounts to replacing the field $\vec{H}$ in Eq. (1) by an effective field which is the sum of the applied field and a term proportional to the magnetization of the specimen, i.e.,

$$\vec{H}_{eff} = \vec{H} + n\vec{M}\;. \tag{6}$$

For weak effective fields, we may write $\vec{M} = \chi^0 \vec{H}_{eff}$ where χ^0 refers to a system of noninteracting ions and is given either by Eq. (4) or Eq. (5). For weak applied fields and temperatures where no spontaneous order occurs we can also write $\vec{M} = \chi\vec{H}$, where χ is the initial susceptibility of a system of interacting ions. Thus $\chi = \vec{M}/\vec{H} = \chi^0(1 + n\chi)$ and finally either

$$\chi_{\parallel} = \chi_{\parallel}^0/(1 - n\chi_{\parallel}^0) \tag{7}$$

or

$$\chi_{\perp} = \chi_{\perp}^0/(1 - n\chi_{\perp}^0)\;. \tag{8}$$

A least-squares fitting of all the data with Eqs. (7) and (8) yields $g = 2.25$, $D/k = 0.64$ K, and $n = -0.02$ mole/emu. This analysis, while not changing the zero-field splitting significantly, does suggest the presence of a weak molecular field of antiferromagnetic sign. At the same time, the splitting factor g has been made larger and brought closer to the value typical[27] of many other salts of Ni^{++}. The fitted susceptibilities obtained by this procedure are shown as solid curves in Fig. 3.

It is sometimes useful to consider molecular field coupling constants in more specific terms. If the interaction of the ith Ni^{++} ion with z nearest neighbors occurs via isotropic exchange $J\sum_{f=1}^{z}\vec{S}_i \cdot \vec{S}_f$, the molecular field term in Eq. (6) may be written[28] as $zJ\langle\vec{S}\rangle/g\mu_B$, where $\langle\vec{S}\rangle$ is a statistical average of $\vec{S}$. Since the magnetization $\vec{M} = Ng\mu_B\langle\vec{S}\rangle$ we can relate the coupling constant n to the exchange integral by the expression $n = zJ/Ng^2\mu_B^2$. In the present case, this would yield $z|J| = 5.2 \times 10^{-19}$ erg or $0.004k$. This is of comparable magnitude with the exchange interaction inferred[29] from the narrowing of paramagnetic-resonance lines observed in $NiSiF_6 \cdot 6H_2O$ and, recently, in this salt. However, n is small enough and sufficiently uncertain in magnitude that doubt must exist as to its

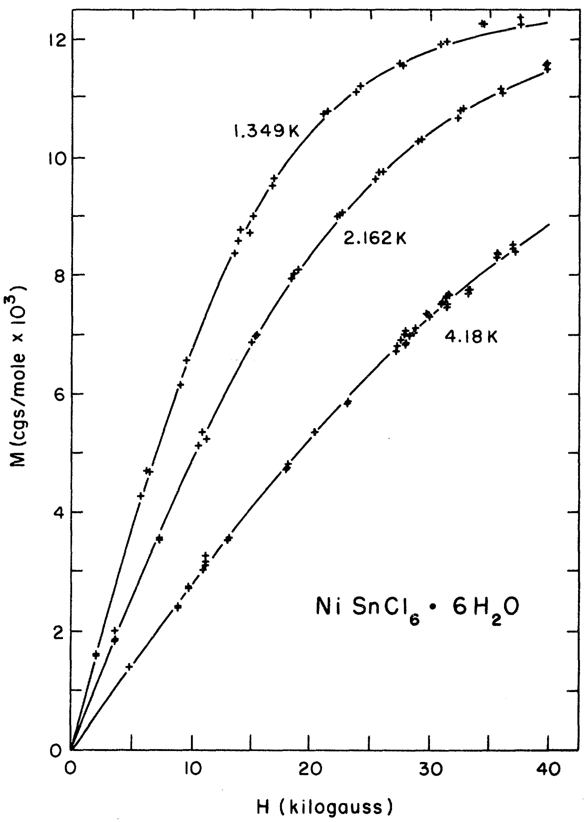

FIG. 4. Magnetization isotherms for $NiSnCl_6 \cdot 6H_2O$ with $H \parallel$ trigonal axis. Solid curves are calculated with $g = 2.25$, $D/k = +0.64$ K, and $n = -0.02$ mole/emu.

microscopic origin. It is possible that it represents the net effect of dipolar and exchange interactions of comparable magnitudes. A crude estimate of the dipolar interaction is given by $S^2 g^2 \mu_B^2 / a^3$. Taking $a = 7.09$ Å in $NiSnCl_6 \cdot 6H_2O$, this amounts to ~ $0.009k$, suggesting that the dipolar contribution is very important if not dominant. Whatever its origin, this interaction is probably "subcritical" in the sense in which we have used that term in our introductory remarks.

Magnetization

Magnetization isotherms measured at three temperatures in the liquid-He^4 region with the field applied parallel to the trigonal axis are shown in Fig. 4. The effects of the zero-field splitting of the Ni^{++} ion ground state are not grossly evident in these results since $kT > D$. However, at the lowest temperatures and at fields less than or comparable with the crossing field $H_c \sim D/g\mu_B \sim 4.2$ kOe quite significant departures from simple Brillouin behavior are noticeable. In calculating theoretical isotherms for noninteracting Ni^{++} ions one uses the field-dependent energies of Eq. (2) and easily obtains

$$M_{\parallel} = \frac{2N_0 g \mu_B \sinh(g\mu_B H_{\parallel}/kT)}{e^{D/kT} + 2\cosh(g\mu_B H_{\parallel}/kT)} . \qquad (9)$$

In order to allow for the molecular field interaction effects it is necessary simply to replace H in this equation with the effective field of Eq. (6). The resulting transcendental equation can be solved numerically by computer for self-consistent values of $M_{\parallel}$ as a function of T and $H_{\parallel}$. This has been done using the values of g, D, and n obtained above by fitting the initial susceptibility data. The calculated isotherms are shown as solid lines in Fig. 4. They reproduce the data to within the experimental uncertainty indicated by the scatter of the measured values. Thus magnetization data in fields up to ~ 40 kOe confirm conclusions drawn from observations at essentially zero field.

Heat Capacity

The heat capacity of a 22.2449-g polycrystalline specimen contained in a copper capsule was measured by the method of discontinuous heating between 0.375 and 4.2 K. In the upper portion of this range the heat capacity of the sample material is a relatively small fraction of the measured total and thus subject to large uncertainties. We therefore report only those data taken below ~ 1.2 K where the capsule correction amounts to ~ 10% or less of the measured quantity. These are shown as crosses in Fig. 5 and are tabulated in Table I.

We have also measured the heat capacity of a 6.7269-g single crystal of $NiSnCl_6 \cdot 6H_2O$ between ~ 0.5 and 4.2 K. The need to use He gas for heat transfer in cooling and thermometer calibration with this specimen restricted the range of reliable data to the region above ~ 0.6 K. Several points taken below that temperature were anomalously high, apparently as a result of the desorption of He gas from the specimen during the heating cycle. Above ~ 0.6 K the single-crystal and polycrystalline data are in reasonable agreement. The ratio of the heat capacities of sample and sample holder was quite favorable over the entire range covered by the single-crystal measurements. These results are shown as solid circles in Fig. 5 and summarized in Table II.

We see in Fig. 5 what is evidently the high-temperature side of an anomaly. If our conclusions from the magnetic results are correct, this anomaly should be of the rounded Schottky type and should have its maximum near 0.25 K. In order to draw quantitative conclusions about the spin system from these data it is necessary to isolate the magnetic contribution to the heat capacity by subtracting the lattice contribution from the measured C_p values. We can estimate the lattice part by assuming it to be separable from the magnetic contribution and to vary as T^3 at temperatures high

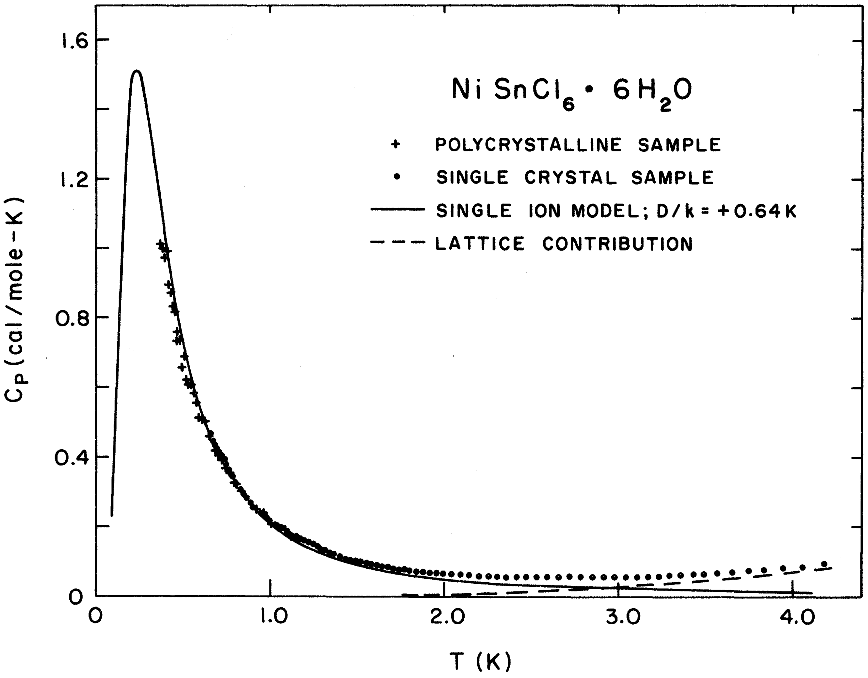

FIG. 5. Observed heat capacity of $NiSnCl_6 \cdot 6H_2O$ between 0.35 and 4.2 K with theoretical curve for $D/k = +0.64$ K (solid line).

enough that the latter varies as T^{-2}, i.e.,

$$C_p \approx aT^3 + bT^{-2} \ . \tag{10}$$

A plot of C_pT^2 vs T^5 gives a good straight line between ~ 2 and 4.2 K. Fitting Eq. (10) to this line using a least-squares procedure one finds $a = 1.056 \times 10^{-3}$ cal/mole K^4 and $b = 0.236$ cal K/mole. The estimated lattice correction aT^3 is shown as a dashed curve in Fig. 5 and has been subtracted from all the data to give the magnetic heat capacity C_{mag}.

If, as has been suggested above, the interactions in $NiSnCl_6 \cdot 6H_2O$ can be represented by a molecular field and are subcritical in magnitude, then, in the absence of an applied field, $\langle \vec{S} \rangle$ will be zero at all temperatures. The appropriate spin Hamiltonian and energy eigenvalues are then given by Eqs. (1) and (2) with $\vec{H} = 0$. A theoretical expression for C_{mag} is easily calculated, namely,

$$\frac{C_{\text{mag}}}{R} = 2\left(\frac{D}{kT}\right)^2 \frac{e^{D/kT}}{(e^{D/kT}+2)^2} \ . \tag{11}$$

This equation has been fitted to the corrected data by a least-squares technique. Using only the data of Table I (polycrystalline sample) the best fit is obtained with $D/k = +0.62$ K. The single-crystal data of Table II alone yield a slightly higher value, $D/k = +0.65$ K. In Fig. 5 the calculated Schottky anomaly for $D/k = +0.64$ K is shown as a solid curve which represents the measured C_p itself quite well once the lattice heat capacity has become negligibly small. While the lowest data points lie slightly below this curve, the discrepancy is comparable with the uncertainty in our temperature scale in this region.

In general, the heat-capacity results appear to be completely consistent with conclusions about the ground-state splitting drawn from the magnetic observations. Recent paramagnetic-resonance measurements[18] at 4.2 K also give $|D|/k = 0.65$ K. The resonance work reveals, in addition, the reduction of the magnitude of D with rising temperature, the functional dependence being rather similar to that observed earlier in $NiSiF_6 \cdot 6H_2O$. There is, however, a most important difference. In the fluosilicate, D is always negative at ordinary pressures.[15] In the chlorostannate, D is positive up to 338 K where it passes through zero. D then assumes negative values with further increase in temperature. The reported[17] negative values of D below room temperature are not confirmed.

Magnetocaloric Effect

Having established that the ground-state triplet of Ni^{++} in $NiSnCl_6 \cdot 6H_2O$ is split into a lower singlet and an upper doublet, we now consider briefly the anticipated magnetocaloric properties of this salt. Ignoring the heat capacity of the lattice vibrations, we have calculated several isentropic curves in a portion of the H, T plane for a spherical crystal of $NiSnCl_6 \cdot 6H_2O$. The single-ion energy levels were those of Eqs. (2) and (3). Interaction effects were included in a molecular field approximation using Eq. (6). The parameters D, g, n obtained in the fitting of the magnetic susceptibility were used in

TABLE I. Specific heat of $NiSnCl_6 \cdot 6H_2O$ (polycrystalline form). C_p is given in cal/mole K and T in K.

T	C_p	T	C_p	T	C_p
0.375	1.011	0.537	0.607	0.840	0.303
0.388	0.989	0.549	0.607	0.866	0.290
0.397	0.970	0.562	0.583	0.895	0.270
0.407	0.990	0.576	0.558	0.926	0.253
0.416	0.893	0.592	0.515	0.961	0.241
0.426	0.898	0.609	0.504	1.000	0.215
0.435	0.873	0.628	0.501	1.039	0.206
0.445	0.834	0.649	0.461	1.078	0.191
0.457	0.818	0.672	0.420	1.115	0.175
0.467	0.731	0.694	0.423	1.152	0.175
0.477	0.757	0.717	0.395		
0.488	0.732	0.741	0.373		
0.500	0.659	0.765	0.356		
0.511	0.690	0.794	0.324		
0.523	0.621	0.817	0.323		

TABLE II. Specific heat of $NiSnCl_6 \cdot 6H_2O$ (single-crystal form).

T	C_p	T	C_p	T	C_p
0.631	0.506	1.177	0.167	2.146	0.060
0.651	0.480	1.199	0.163	2.205	0.059
0.663	0.470	1.221	0.158	2.263	0.057
0.676	0.445	1.245	0.151	2.310	0.055
0.689	0.436	1.269	0.142	2.358	0.055
0.701	0.424	1.294	0.137	2.422	0.055
0.716	0.418	1.319	0.133	2.474	0.054
0.729	0.405	1.345	0.129	2.531	0.053
0.743	0.395	1.372	0.124	2.591	0.054
0.757	0.372	1.401	0.117	2.658	0.054
0.771	0.360	1.429	0.111	2.719	0.054
0.786	0.349	1.459	0.109	2.781	0.055
0.801	0.336	1.489	0.103	2.846	0.054
0.816	0.322	1.519	0.100	2.912	0.054
0.832	0.304	1.550	0.097	2.978	0.056
0.848	0.292	1.580	0.094	3.041	0.056
0.867	0.283	1.613	0.090	3.104	0.056
0.886	0.272	1.644	0.087	3.169	0.058
0.905	0.260	1.676	0.084	3.232	0.058
0.927	0.255	1.709	0.082	3.294	0.060
0.947	0.241	1.741	0.078	3.356	0.060
0.967	0.232	1.774	0.078	3.423	0.061
0.988	0.222	1.806	0.075	3.494	0.063
1.008	0.217	1.843	0.071	3.571	0.065
1.031	0.209	1.879	0.070	3.653	0.069
1.055	0.200	1.917	0.069	3.742	0.072
1.082	0.189	1.956	0.066	3.838	0.075
1.107	0.184	1.999	0.065	3.943	0.080
1.131	0.178	2.045	0.063	4.060	0.085
1.154	0.175	2.095	0.062	4.184	0.091

these calculations. The results for $H\parallel$ trigonal axis and several initial temperatures T_i ($H=0$) are shown in Fig. 6 as solid curves. Because of the small singlet-doublet separation ($D/k = 0.64$ K) cooling by adiabatic magnetization becomes possible only for $T_i \lesssim 0.35$ K. In this simplified scheme, however, quite substantial cooling occurs for $T_i \lesssim 0.30$ K, the lowest temperature being reached when $H_\parallel \approx D/g\mu_B = 4.2$ kOe. If interaction had been completely ignored, i.e., if $n = 0$, then each isentrope with $T_i \lesssim 0.3$ K would have shown a cusp at $H_\parallel = 4.2$ kOe and $T = 0$ K. In the present calculation, the effect of interaction is to produce a gap in the isentrope at 0 K whose width depends on the strength of the interaction and T_i. It is within this range of fields about $D/g\mu_B$ that long-range spin order might be expected to occur if the coupled system were three dimensional.[8,9] A more detailed molecular field calculation would be expected to give continuous isentropes in this region with flat minima parallel to the H axis at $T_{\min} > 0$ K. The locus of extrema of the flat segments of these isentropes would constitute a boundary between ordered and disordered phases as shown in Fig. 2. In the absence of misalignment or other effects causing level mixing, the lowest temperature attainable by adiabatic magnetization from a given T_i would be $T_{\min}$ as fixed by the interaction of the Ni^{++} ions.

Assuming that we wish to achieve low temperatures and an ordered spin state by adiabatic magnetization of $NiSnCl_6 \cdot 6H_2O$ from zero field, an initial temperature $T_i \lesssim 0.30$ K must first be achieved. This is near the lower limit usually available with liquid He^3. Referring to the dashed line in Fig. 6 which represents an isentropic curve for $H\perp$ trigonal axis, we see that $T_i = 0.30$ K can be reached by adiabatic demagnetization from a temperature ~ 1 K and a field ~ 9 kOe in the perpendicular orientation. At $H = 0$ and $T_i = 0.30$ K, with the crystal still adiabatically isolated, one could then rotate the magnet into a parallel orientation and continue the cooling by increasing the field until $T_{\min}$ had been achieved.

We have used the same single-crystal specimen employed in the heat-capacity measurements to carry out some exploratory magnetocaloric measurements on $NiSnCl_6 \cdot 6H_2O$. Unfortunately, it was not practical to rotate either the magnet or the specimen in this work, to reduce the applied field to zero, or to achieve starting temperatures below about 0.45 K. We have, therefore, traced out portions of some experimental isentropic curves initially cooling the specimen by adiabatic demagnetization from fields greater than 4.2 kOe, starting at the lowest temperature reached by thermal contact with liquid He^3.

Figure 7 shows two of the curves observed by reducing the field by discrete amounts at a uni-

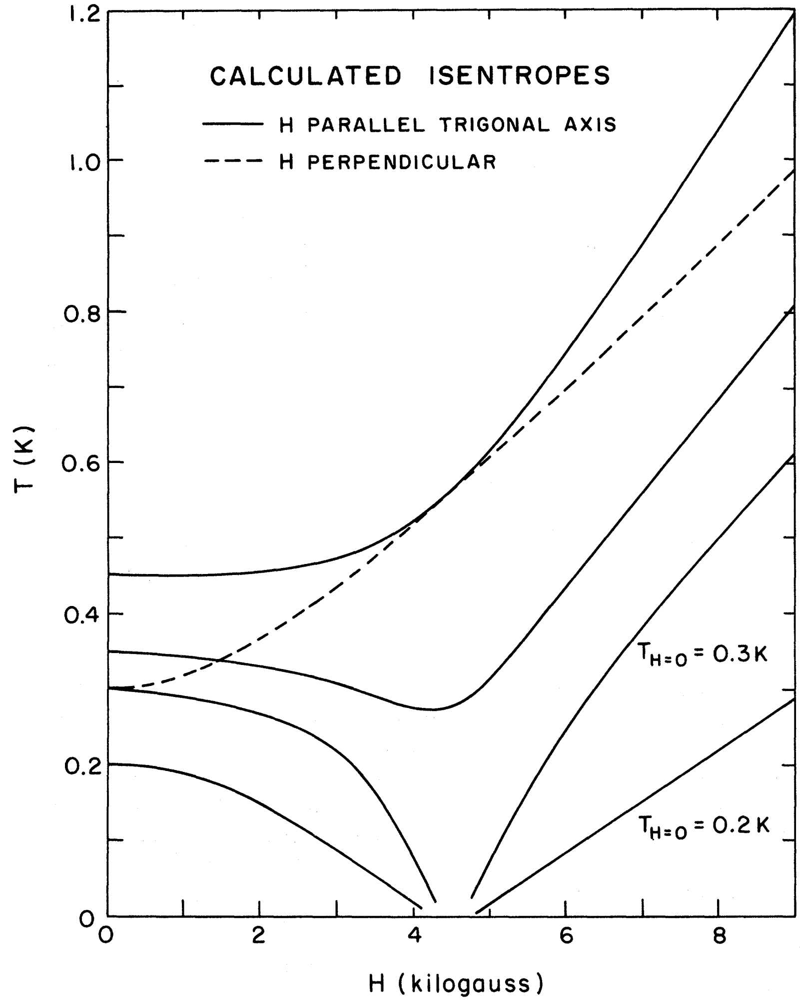

FIG. 6. Calculated isentropic curves for spherical crystal of $NiSnCl_6 \cdot 6H_2O$ with $g = 2.25$, $D/k = +0.64$ K, and $n = -0.02$ mole/emu.

form rate and recording the steady temperature achieved after completion of each field change. Starting at $H = 7$ kOe and $T = 0.47$ K, the path indicated by open circles was followed through a pronounced minimum at $H \sim 4.2$ kOe and $T \sim 0.33$ K and up again to $T \sim 0.36$ K at $H \sim 3.4$ kOe. The field at which $T_{\min}$ is reached is, as predicted, the crossover field $H_c = D/g\mu_B = 4.2$ kOe. Comparing this empirical isentropic curve with the third calculated curve from the bottom of Fig. 6, we note a semiquantitative agreement.

Starting at $H \sim 9.2$ kOe and $T \sim 0.45$ K, the path indicated in Fig. 7 by solid circles was mapped out. The minimum occurs at roughly the same field value but is now rather broad and flat. Again a region of negative slope is reached at the lowest fields. It is here, of course, that the system cools on adiabatic magnetization. The curve indicated by crosses in Fig. 7 was actually obtained by adiabatically increasing the field from an (H, T) point originally reached in a demagnetization process. Cooling by adiabatic magnetization has been clearly seen along the initial portion of this curve and others like it.

It is tempting to associate the broad flat minima seen in the lower isentropic curves of Fig. 7 with the appearance of an ordered phase of the kind mentioned above. There are a number of reasons, however, why such a conclusion may be premature. It must be remembered that the temperatures of all points in Fig. 7 are expressed in terms of an extrapolated scale whose validity is quite difficult to assess. At the lowest apparent temperatures, ~ 0.30 K, the resistance of the carbon thermometer has reached very high values (~ 10^7 Ω) and problems of measurement arise, among them the question of leakage. It is possible, for example, that the real temperatures of some of the points may be much lower than those indicated and that the minima are not as flat or broad as they appear.

Another difficulty is the possible misalignment of the field and the trigonal axis of the crystal. A crude estimate suggests that misalignment of 2°, the uncertainty in orientation of the crystal, could

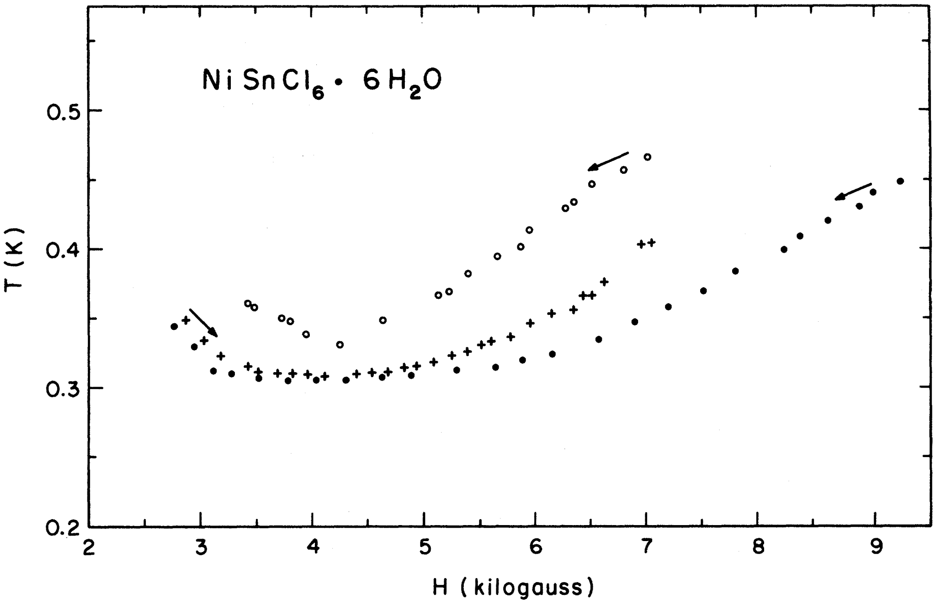

FIG. 7. Some empirical isentropic curves for $NiSnCl_6 \cdot 6H_2O$. Arrows indicate whether data were taken with increasing or decreasing field.

broaden the minimum in an isentropic curve and affect T_{min} to roughly the same extent as interactions of the magnitude implied by our fitting of the susceptibility data. Referring to Fig. 6, we see that for a molecular field constant $n = 0.02$ mole/emu, interaction alone might be expected to cause an isentrope to be flat over a field interval of ~ 1 kOe at the lowest temperatures. While the lower curves of Fig. 6 are flat over roughly such a range of field, $T_{min} \sim 0.3$ K seems a rather high temperature for the full width to appear unless the interactions are stronger than previously estimated or other broadening mechanisms, real or apparent, are present. Thus, while the two lower isentropic curves of Fig. 7 do have the general characteristics expected for a system which orders only in a certain range of applied field, not all sources of experimental complications have been eliminated. Further magnetic and thermal studies of $NiSnCl_6 \cdot 6H_2O$, employing a He^3-He^4 dilution refrigerator to maintain temperatures below ~ 0.5 K, have been initiated in this laboratory to establish whether or not this interesting ordered phase actually exists.

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[1] C. Kittel, Physica Suppl. 24, S88 (1958).

[2] W. P. Wolf, Phys. Rev. 115, 1196 (1959).

[3] S. A. Friedberg and C. A. Raquet, J. Appl. Phys. 39, 1132 (1968).

[4] K. Amaya, Y. Tokunaga, R. Yamada, Y. Ajiro, and T. Haseda, Phys. Letters 28A, 732 (1969).

[5] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1950).

[6] For example, α-$NiSO_4 \cdot 6H_2O$; see T. Watanabe, J. Phys. Soc. Japan 17, 1856 (1962); J. W. Stout and W. B. Hadley, J. Chem. Phys. 40, 55, (1964).

[7] T. Moriya, Phys. Rev. 117, 635 (1960).

[8] T. Tsuneto and T. Murao, Physica 51, 186 (1971).

[9] The closely related problem of a system of elements with a lower singlet and an upper triplet has been treated by M. Tachiki and T. Yamada, J. Phys. Soc. Japan 28, 1413 (1970); Progr. Theoret. Phys. (Kyoto) Suppl. 46, 291 (1970).

[10] M. W. van Tol, L. S. J. M. Henkens, and N. J. Poulis, Phys. Rev. Letters 27, 739 (1971).

[11] A. Herweijer and S. A. Friedberg, Phys. Rev. B 4, 4009 (1971).

[12] L. Pauling, Z. Krist. 72, 452 (1930).

[13] R. P. Penrose and K. W. H. Stevens, Proc. Phys. Soc. (London) A63, 29 (1950).

[14] J. Becquerel and J. van den Handel, Physica 6, 1034 (1939).

[15] W. M. Walsh, Jr., Phys. Rev. 114, 1473 (1959).

[16] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1965), Vol. 3, p. 796.

[17] B. D. Bhattacharyya and M. Majumdar, Ind. J. Phys. 40, 549 (1966).

[18] Y. Ajiro, N. S. VanderVen, and S. A. Friedberg, Bull. Am. Phys. Soc. 17, 262 (1972).

[19] T. Smith and S. A. Friedberg, Phys. Rev. 176, 660 (1968).

[20] B. E. Myers, L. Berger, and S. A. Friedberg, J. Appl. Phys. 40, 1149 (1969).

[21] C. A. Raquet, Ph.D. dissertation (Carnegie Institute of Technology, 1967) (unpublished).

[22] L. G. Polgar, Ph.D. dissertation (Carnegie-Mellon University, 1970) (unpublished).

[23] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U.S.) 68A, 579 (1964).

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

[25] J. R. Clement, E. H. Quinnell, M. C. Steele, R. A. Hein, and R. L. Dolecek, Rev. Sci. Instr. 24, 545 (1953).

[26] D. L. Decker and H. Laquer, Cryogenics 9, 481 (1969).

[27] K. D. Bowers and J. Owens, Rept. Progr. Phys. 18, 304 (1955).

[28] See, for example, T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. 4, 1 (1955).

[29] E. Ishiguro, K. Kambe, and T. Usui, Physica 17, 310 (1951).

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Low-Temperature Heat Capacity of $Ni(CH_3COO)_2 \cdot 4H_2O^\dagger$

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The heat capacity of $Ni(CH_3COO)_2 \cdot 4H_2O$ has been measured between 0.43 and 10.73 K revealing a Schottky anomaly with $C_{p\,\mathrm{max}} = 1.182$ cal/mole K at $T_{\mathrm{max}} = 1.98$ K. An octahedral crystal field with axial and rhombic distortions plus spin-orbit interaction split the triplet ground state completely, the upper components lying $3.52k$ and $8.06k$ above the lowest. The lattice contribution to C_p is estimated to be $3.69 \times 10^{-4} T^3$ cal/mole K. Comparison of the ground-state splittings with those inferred from magnetic-susceptibility data suggests the presence of a small interaction between Ni^{++} ions. This is described by an antiferromagnetic molecular-field coefficient $A/k = +0.08$ K which may be largely of dipolar origin.

INTRODUCTION

Nickel acetate tetrahydrate forms monoclinic crystals belonging[1] to the space group $P2_1/c$. The unit cell contains two formula units and has the dimensions[1,2] $a = 4.75$ Å, $b = 11.77$ Å, and $c = 8.44$ Å with $\beta = 93°36'$. Each Ni^{++} ion is octahedrally coordinated by six oxygen atoms; four of these belong to water molecules and the others to carboxyl groups.

Measurements of the magnetic susceptibility of powdered $Ni(CH_3COO)_2 \cdot 4H_2O$ between 1.3 and 20 K [3] and from 0.35 to 4.2 K [4] give no obvious evidence of significant coupling among Ni^{++} ions. The data could be well described by a single-ion model in which the octahedral environment exhibits both axial and rhombic distortions. These, together with the spin-orbit interaction, fully lift the threefold spin degeneracy of the ^3A ground state. The two upper levels were found[4] to lie $3.82k$ and $7.82k$ above the lowest. The average g factor was 2.24. Mookherji and Mathur[5] have measured the single-crystal susceptibilities of this salt between 85 and 300 K. They interpret their results by assuming only a tetragonal distortion of the crystal field and conclude that an upper doublet lies $\sim 12k$ above a lower singlet. It is not clear whether any attempt was made to include a rhombic distortion in this analysis. In any event, the effects of additional splitting of the ground state would not be readily observable at such relatively high temperatures. Apparent differences between splittings deduced from high- and low-temperature magnetic data may indicate some temperature variation of the crystal field in this system, but this is not firmly established. Preliminary results of single-crystal susceptibility measurements[6] performed in this laboratory at low temperatures confirm conclusions drawn from the powder data in that region.

We have measured the heat capacity of $Ni(CH_3COO)_2 \cdot 4H_2O$ at low temperatures in order to get an independent determination of the zero-field splitting of the ground state of the Ni^{++} ion. Since the splitting evidently leaves a singlet as the lowest state, the possibility arises that there might be significant interionic interaction in this material which could be "subcritical" in the sense that it would be too small relative to the splitting to produce cooperative long-range spin order at any temperature.[7] In the simplest molecular-field picture, subcritical interactions contribute to the effective magnetic field at a Ni^{++} ion when an external field is applied. While in first approximation both the initial susceptibility and zero-field heat capacity would appear to be those of a sys-