Magnetic and thermal behavior of NiSnCl$_6$·6H$_2$O at low temperatures

D. L. Meier,* M. Karnezos,† and S. A. Friedberg

Physics Department, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 24 February 1983)

NiSnCl$_6$·6H$_2$O crystals have a trigonal structure containing one trigonally distorted [Ni(H$_2$O)$_6$]$^{2+}$ complex per unit cell. We have measured the magnetic susceptibilities $\chi_{||}$ and $\chi_\perp$ and the heat capacity C_P of single-crystal specimens of this salt down to ~0.06 K in a ^{3}He-^{4}He dilution refrigerator. The low- (zero-) field data are well described by a model in which the $^3A_{2g}$ ground state of [Ni(H$_2$O)$_6$]$^{2+}$ is split into a lower singlet separated from an excited doublet by $D/k = 0.576$ K, and significant antiferromagnetic interionic interactions exist which are too small relative to D to produce long-range spin order. Using both simple mean-field and Oguchi approximations, we have determined the parameters D, $g(=2.24)$, and $zJ/k(=-0.044$ K). Some anisotropy of the subcritical coupling constant, probably of dipolar origin, is inferred from the susceptibility results. Magnetocaloric effect and heat capacity were measured for single crystals with $\vec{H}$ parallel to the trigonal axis. Cooling by adiabatic magnetization, followed by level crossing at $H'_c = 4100$ Oe, was observed. However, attempts to observe field-induced long-range spin ordering were not successful.

I. INTRODUCTION

Nickel chlorostannate hexahydrate, NiSnCl$_6$·6H$_2$O, forms trigonal (rhombohedral) crystals belonging[1] to the space group $R\bar{3}$. The rhombohedral unit cell (parameters $a_0 = 7.09$ Å and $\alpha = 96°45'$) contains a single [Ni(H$_2$O)$_6$]$^{2+}$ octahedral complex trigonally distorted along the trigonal axis of the crystal. The axial distortion of the crystal field together with spin-orbit interaction splits the $^3A_{2g}$ ground state of the complex into a singlet and a doublet. We have shown,[2] through measurements of magnetic susceptibility, magnetization, heat capacity, and electron-spin resonance,[3] that in NiSnCl$_6$·6H$_2$O this splitting is such as to leave the singlet ~0.6k below the doublet at temperatures below 4.2 K.

We were able to fit these early measurements on NiSnCl$_6$·6H$_2$O, at least qualitatively, with a single-ion spin Hamiltonian for $S = 1$,

$$H = DS_z^2 + g_{||}\mu_B S_z H_z + g_\perp \mu_B (S_x H_x + S_y H_y) , \qquad (1)$$

where the z direction is along the trigonal axis, $g_{||} \sim g_\perp = g = 2.24$, and the zero-field splitting $D/k \cong +0.6$ K. With the magnetic field $\vec{H}||\hat{z}$ the energy eigenvalues of Eq. (1) may be written

$$W_1 = D - g_{||}\mu_B H_{||}, \quad W_2 = D + g_{||}\mu_B H_{||}, \quad W_3 = 0 , \qquad (2)$$

while for $\vec{H}\perp\hat{z}$ they are

$$W_1 = D, \quad W_2 = \frac{1}{2}[D - (D^2 + 4g_\perp^2\mu_B^2 H_\perp^2)^{1/2}] ,$$

$$W_3 = \frac{1}{2}[D + (D^2 + 4g_\perp^2\mu_B^2 H_\perp^2)^{1/2}] . \qquad (3)$$

These familiar results are illustrated graphically in Fig. 1 for $D > 0$.

With these eigenvalues it is a straightforward matter to

calculate theoretical expressions for each of the measured quantities. Thus we find for the susceptibility in a vanishing field along the trigonal axis,

$$\chi_{||}^0 = \frac{2N_0 g_{||}^2\mu_B^2}{kT} \frac{1}{e^{D/kT}+2} , \qquad (4)$$

and perpendicular to the trigonal axis,

$$\chi_\perp^0 = \frac{2N_0 g_\perp^2\mu_B^2}{D} \frac{e^{D/kT}-1}{e^{D/kT}+2} . \qquad (5)$$

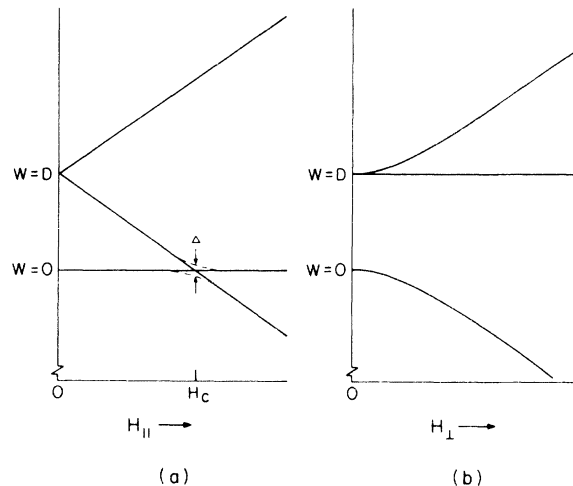The isothermal magnetization measured along the trigonal axis in a field $H_{||}$ is given by

FIG. 1. Field dependence (schematic) of the eigenvalues of the spin Hamiltonian $H = DS_z^2 + g\mu_B\vec{S}\cdot\vec{H}$ for $S = 1$ and $D > 0$. (a) $\vec{H}$ parallel to the trigonal axis with effect of small misalignment shown by dashed curve; (b) $\vec{H}$ perpendicular to the trigonal axis.

$$M_{||} = \frac{2N_0 g_{||}\mu_B \sinh(g_{||}\mu_B H_{||}/kT)}{e^{D/kT} + 2\cosh(g_{||}\mu_B H_{||}/kT}, \tag{6}$$

while the contribution to the heat capacity of N_0 independent Ni^{2+} ions in zero field is just

$$\frac{C_0(\text{mag})}{N_0 k} = 2\left[\frac{D}{kT}\right]^2 \frac{e^{D/kT}}{(e^{D/kT}+2)^2}. \tag{7}$$

Although Eqs. (4)–(7) could fit our earlier static data on NiSnCl$_6$·6H$_2$O between ~0.4 and 4.2 K in a qualitative or semiquantitative fashion, small but significant systematic discrepancies were evident. These can be removed, at least for the susceptibility and magnetization, by allowing the Ni^{2+} ions to interact with one another in a a simple mean-field approximation. This is accomplished by replacing the applied field $\vec{H}$ with an effective field $\vec{H}_{\text{eff}} = \vec{H} + n\vec{M}$, where $\vec{M}$ is the magnetization. Then the susceptibilities of a system of weakly interacting ions in the absence of spontaneous order are expressed in terms of the results given above, Eqs. (4) and (5), for noninteracting ions and the mean-field coupling constant n as

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

or

$$\chi_\perp = \chi_\perp^0/(1 - n\chi_\perp^0). \tag{9}$$

Similarly, the insertion of $\vec{H}_{\text{eff}}$ in Eq. (6) gives a transcendental equation which can be solved numerically for self-consistent values of $M_{||}$ as a function of T and H for a given value of n. The mean-field coupling constant determined by fitting the original data on $\chi_{||}$, $\chi_\perp$, and $M_{||}$ with these results is $n = -0.02$ mole/emu. It is antiferromagnetic in sign and of subcritical magnitude, i.e., too small relative to $|D|$ to be expected[4] to cause spontaneous long-range magnetic order to occur above 0 K, at least in the absence of an applied magnetic field.

As has been pointed out,[2] the fact that NiSnCl$_6$·6H$_2$O is a system of crystallographically equivalent Ni^{2+} ions with spin $S = 1$ having singlet ground states, low-lying excited magnetic doublets, and subcritical but nonnegligible interionic interactions makes it an interesting object for study at low temperatures. As is evident in Fig. 1(a), for example, a magnetic field parallel to the trigonal axis of an isolated crystal initially at a temperature $T \ll D/k$ will produce cooling when increased adiabatically so long as $H_{||} < H_c = D/g\mu_B$. At H_c, the lower component of the excited doublet nominally crosses the singlet ground state. Only when $H_{||} > H_c$ should we observe the heating which accompanies adiabatic magnetization in conventional paramagnets. Qualitative evidence of this effect in NiSnCl$_6$·6H$_2$O has, in fact, already been reported.[2] Of perhaps greater interest, however, is the possibility that a crystal of NiSnCl$_6$·6H$_2$O in a field $H_{||} \sim H_c$ cooled to a temperature such that kT is of the order of the interionic coupling energy may exhibit long-range spin order. Such ordering is unusual in that it involves only components of the spin perpendicular to the applied field and occurs only for fields $H_{||}$ in a well-defined range about H_c. A theory of the process has been given by Tsuneto and Murao.[5]

Most of our earlier data on NiSnCl$_6$·6H$_2$O did not extend below ~0.4 K and were thus limited to temperatures $\gtrsim D/k$. In this paper we wish to report single-crystal measurements down to about 60 mK of the low-field magnetic susceptibilities and of the heat capacity with $H = 0$ and $H_{||} \cong 4$ kOe, as well as some observations of the magnetocaloric effect. These measurements provide more accurate information about the single-ion spin-Hamiltonian parameters D and g and the strength of the interionic coupling in this salt. They can be well-described in terms of a simple model and lend support to more detailed theoretical analyses of excitations in such a system. However, the interactions proved to be too small to permit the observation of field-induced spin ordering at accessible temperatures. Since the preliminary report[6] of some of these results was made, other $S = 1$ compounds of Ni^{2+} with singlet ground states and relatively larger subcritical interactions have been identified. Several of these have now been shown[7-9] to exhibit field-induced spin ordering at convenient values of temperature and applied field.

II. EXPERIMENTAL DETAILS

The single crystals of NiSnCl$_6$·6H$_2$O employed in this work were grown by slow evaporation at 28.0±0.1 °C of an equimolar solution of reagent grade NiCl$_2$·6H$_2$O and SnCl$_4$·5H$_2$O in distilled water. Clear dark-green crystals with linear dimensions up to several centimeters were obtained. The trigonal (c) axis was easily identified by inspection.

All of the measurements to be described were performed in a cryostat cooled by a ^{3}He-^{4}He dilution refrigerator. Interchangeable assemblies were used to adapt the cryostat either for calorimetry or for magnetic susceptibility measurements.[10] Magnetic susceptibilities were determined by a mutual inductance technique at a frequency of 70 Hz, the oscillatory field having an amplitude < 10 Oe. The apparatus employed three matched mutual inductances thermally anchored to the 1-K reservoir of the refrigerator. Thus it was possible in one experiment to measure the susceptibilities of NiSnCl$_6$·6H$_2$O parallel and perpendicular to the trigonal axis, as well as that of a cerium magnesium nitrate (CMN) thermometric sample. All these specimens were mounted within, but not in contact with, their respective coils and thermally linked to the mixing chamber by bundles of insulated copper wires. The data to be reported cover the temperature range 0.069–3.6 K. $\chi_{||}$ and $\chi_\perp$ were measured on crystals weighing 0.3133 and 0.2696 g, respectively. Since a sample of known susceptibility cannot be substituted for the NiSnCl$_6$·6H$_2$O specimens during an experimental run, we have normalized the data to values determined earlier above 0.4 K in a liquid ^{3}He-cooled cryostat where such standardization is possible.

In order to measure heat capacities and magnetocaloric effects, the mutual inductance assembly was removed from the cryostat and replaced with a calorimetric insert. This consists of a supporting frame within which is suspended by thread the single-crystal specimen and a bundle of 3000 #40 Cu wires linking it to the refrigerator mixing chamber via a pincers-type mechanical heat

switch. A Speer 220-Ω, $\frac{1}{2}$-W carbon resistor and a heater winding are embedded in the wire heat link. The carbon thermometer was calibrated, with the heat switch closed, against a CMN thermometer mounted directly on the mixing chamber. The constant of the CMN thermometer was, in turn, determined above 0.5 K by means of a calibrated germanium thermometer also attached to the mixing chamber. The calibration procedure, beginning with establishment of the constant for the CMN thermometer, was repeated after each warming of the cryostat to room temperature. Extrapolating the magnetic scale to ~ 0.050 K, the carbon resistors and CMN thermometer were compared at about 20 points between 0.05 and 4.2 K. These R-T data were fitted with an expression of the form

$$\left[\frac{\log_{10}R}{T} \right]^{1/2} = A + B(\log_{10}R) + C(\log_{10}R)^2 + D(\log_{10}R)^3 .$$

$$(10)$$

The rms deviation of the observed from the calculated temperatures was typically about 1%. Thermometer resistance was measured with an ac bridge employing phase sensitive detection (P.A.R. Model 121) and operating at low current to keep power dissipation within acceptable limits, i.e., $< 10^{-12}$ W at 50 mK.

The lower end of the calorimeter insert and its surrounding vacuum jacket fit into the bore (4.6-cm diameter) of a Nb-Zr superconducting solenoid. The specimen crystal is situated at the center of the solenoid with its trigonal axis and the applied field aligned to within $\sim \pm 3°$. Two crystals were employed in the present measurements: one, in the form of a parallelepiped elongated along the trigonal axis, weighed 3.97 g, and the other, weighing 11.57 g, was ellipsoidal with its long axis parallel to the trigonal direction and a calculated demagnetizing factor $N = 3.52$. The carbon resistance thermometer was situated outside the solenoid. Magnetoresistive effects due to the weak fringe field of the magnet were small. An empirical correction applied to the resistance data was significant only at the highest fields where it amounted to a few percent. All heat-capacity data reported below were obtained by the discontinuous heating (heat-pulse) method.

III. RESULTS AND DISCUSSION

A. Zero-field behavior

1. Magnetic susceptibility

The magnetic susceptibilities of NiSnCl$_6$·6H$_2$O measured parallel and perpendicular to the trigonal axis at temperatures down to 0.069 K are shown in Fig. 2. In the region above 0.4 K these results agree with our previously published data[2] extending down to that temperature. As mentioned in Ref. 2, there has been no suggestion of anisotropy in $\chi_\perp$ in measurements on several different specimens. The data of Fig. 2 exhibit two very important features not previously observed. $\chi_\parallel$ is now found to pass through a rounded maximum at ~ 0.4 K and then to approach zero as $T \rightarrow 0$. $\chi_\perp$, on the other hand, continues to increase below 0.4 K but has become nearly temperature independent at 0.069 K. Qualitatively, this is just the
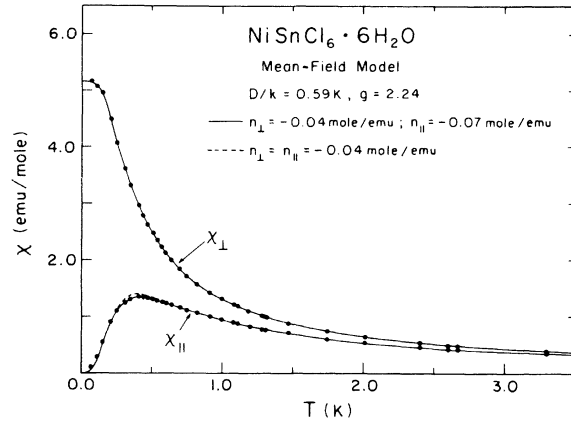

FIG. 2. Magnetic susceptibilities of single-crystal NiSnCl$_6$·6H$_2$O measured parallel and perpendicular to the trigonal axis. Solid curves are calculated for the mean-field model using $D/k = +0.59$ K, $g = 2.24$, $n_\perp = -0.04$ mole/emu, and $n_\parallel = -0.07$ mole/emu. Dashed curve shows $\chi_\parallel$ calculated with an isotropic coupling constant $n_\parallel = n_\perp = -0.04$ mole/emu.

behavior expected of a system of $S = 1$ ions obeying the single-ion spin Hamiltonian, Eq. (1), with $D > 0$ and a singlet ground state. As indicated in Fig. 1(a), a field applied along the trigonal axis has no effect on the singlet so that if $T \ll D/k$ and no other state is populated, $\chi_\parallel \cong 0$. Referring to Fig. 1(b), we see that a perpendicular field will depress the ground state and induce a temperature-independent moment by a mechanism which is the spin analog of Van Vleck paramagnetism. Thus as $T \rightarrow 0$, $\chi_\perp$ should approach a constant nonzero value. According to Fig. 2, this is what is observed.

Before attempting an analysis of the data of Fig. 2, we should estimate the magnitudes of the temperature-independent susceptibility contributions arising from the diamagnetism of the constituent atoms in the crystal and from the Van Vleck paramagnetism due to excited orbital states. Adding to the spin Hamiltonian, Eq. (1), the quadratic Zeeman term,[11] the Van Vleck (VV) susceptibility is easily derived. It may be written in the form

$$\chi_{VV} = (N_0 \mu_B^2 / \lambda)(2 - g) .$$

$$(11)$$

Taking $\lambda \cong -270$ cm^{-1} and using the splitting factor determined by paramagnetic resonance measurements at low temperatures,[3] $g = 2.26$, one finds $\chi_{VV} = 2.55 \times 10^{-4}$ emu/mole. The diamagnetic contribution may be estimated from the tabulated values[12] for the component ions and ligands to be -2.72×10^{-4} emu/mole. The net temperature-independent susceptibility from these two sources is thus -0.17×10^{-4} emu/mole and is quite negligible in the temperature region of interest in the present work.

Not only does the limiting behavior of $\chi_\parallel(T)$ and $\chi_\perp(T)$ as $T \rightarrow 0$ agree qualitatively with expectations based on the single-ion spin Hamiltonian, Eq. (1) for $D > 0$, but the data of Fig. 2 give no obvious suggestion of the occurrence of a magnetic ordering transition at any temperature. These facts support our earlier conclusion that interactions among Ni^{2+} ions in NiSnCl$_6$·H$_2$O are of subcritical

strength. As a first approximation, therefore, we assume the interactions to be negligible and use Eqs. (4) and (5) to fit $\chi_\parallel$ and $\chi_\perp$, respectively. In doing this we further assume that $g_\parallel \cong g_\perp = g$. Justification of this simplification follows from the theory of the spin Hamiltonian[13] according to which $g_\parallel - g_\perp = 2D/\lambda$. In this case, $D \cong 1$ cm^{-1} and $\lambda \cong -270$ cm^{-1} (Ref. 14) so that one expects $g_\parallel - g_\perp \cong -0.007$, which would be quite undetectable in our measurements. The fit of the data of Fig. 2 obtained in this way using a least-squares procedure to optimize the choice of g and D is only qualitatively satisfactory. Systematic discrepancies are noticeable and the g factor giving the best fit is significantly smaller than the value $g = 2.26$ obtained from paramagnetic resonance measurements. The parameter $D/k \cong +0.65$ K determined in this fitting process is comparable in magnitude with earlier values and, of course, of the same sign, indicating that the ground state is a singlet.

In an effort to improve the fit of our data, we have introduced interaction among the Ni²⁺ ions in the simplified mean-field approximation discussed above. A least-squares fit of Eqs. (8) and (9) to the $\chi_\parallel$ and $\chi_\perp$ data yields the parameters $D/k = +0.59 \pm 0.02$ K, $g = 2.24 \pm 0.02$, and $n = -0.04$ mole/ emu. The fitted curves are shown as dashed lines in Fig. 2 and generally reproduce the data quite well. Small systematic discrepancies are, however, found for $\chi_\parallel$ at the lowest temperatures and in the vicinity of the maximum. The fact that the calculated values of $\chi_\parallel$ lie below the data near 0.069 K is probably the result of slight misalignment of the specimen. $\chi_\perp$ is about 40 times larger than $\chi_\parallel$ at this temperature, so that misalignments of only a few degrees could account for the effect. It should be noted that a temperature-independent paramagnetic contribution would also produce such behavior. However, as shown above, the most important contribution of this type, the Van Vleck paramagnetism, is too small by several orders of magnitude.

The small difference between the measured and calculated values of $\chi_\parallel$ near 0.4 K appears to be significant. We find $\chi_\parallel$ in this region to be rather sensitive to the choice of mean-field coupling constant. The fitting of $\chi_\parallel$ and $\chi_\perp$ was repeated allowing n to be anisotropic, i.e., to take on distinct values $n_\parallel$ and $n_\perp$. This procedure yielded, as before, $D/k = 0.59$ K, $g = 2.24$, and $n_\perp = -0.04$ mole/emu. However, now we find $n_\parallel = -0.07$ mole/emu. The solid curves in Fig. 2 have been computed with these parameters. Quantitative agreement with the data has been extended to include the region of the maximum in $\chi_\parallel$.

The fitted parameters of the simple mean-field model are in reasonable agreement with those determined earlier with data taken above 0.4 K. The magnitude of D/k is somewhat ($\sim 8\%$) smaller than before. The coupling constant n, while still of antiferromagnetic sign, has increased significantly. If it is attributed exclusively to isotropic exchange interaction of the form $-2J\sum \vec{S}_i \cdot \vec{S}_j$ for z nearest neighbors, we find $zJ/k = nN_0 g^2 \mu_B^2/2k = -0.036$ K. According to Moriya's criterion,[4] however, the coupling is still of subcritical magnitude since $z|J| < |D|/2$. It must be emphasized that J is at best an "effective" ex-

change constant since the mean field represents some unspecified mixture of exchange interaction (isotropic and anisotropic) and dipolar coupling. If, as has been suggested above, the mean field is actually anisotropic, then $zJ_\parallel = -0.066k$ and $zJ_\perp = -0.036k$. It seems unlikely that anisotropic exchange alone could account for such a difference. However, magnetic dipolar interaction is important in this compound. A crude estimate of its strength is given by $S(S+1)g^2\mu_B^2/a^3$. Taking $a = 7.09$ Å in NiSnCl₆·6H₂O, this amounts to $\sim 0.018k$. Thus the dipolar contribution to the net interaction is a major one and could well be responsible for much of the apparent anisotropy of the effective coupling constant.

2. Heat Capacity

The heat capacity in zero applied field $C_p(H=0)$ of a 3.97-g crystal of NiSnCl₆·6H₂O was measured between 0.066 and 4.6 K. Several independent experimental runs yielded results in excellent agreement. Figure 3 shows the magnetic contribution to the heat capacity $C_p(\text{mag})$ as a function of temperature below 2.2 K. Separation of $C_p(\text{mag})$ from the measured total heat capacity of the specimen and its calorimetric addenda was accomplished approximately by fitting those data in the interval 1.2—4.6 K with an expression of the form

$$C_p = aT + bT^3 + C^0(\text{mag}) . \tag{12}$$

The first two terms represent the electronic and lattice contributions of the addenda as well as the lattice part of the specimen heat capacity. The third term is the heat capacity of N noninteracting Ni²⁺ ions in zero field as given by Eq. (7). In this case it need represent only the high-temperature tail of a Schottky-like anomaly. A good fit was obtained with the zero-field splitting $D/k = +0.58$ K. The difference $C_p - C^0(\text{mag}) = aT + bT^3$ was then assumed to approximate nonmagnetic contributions to the
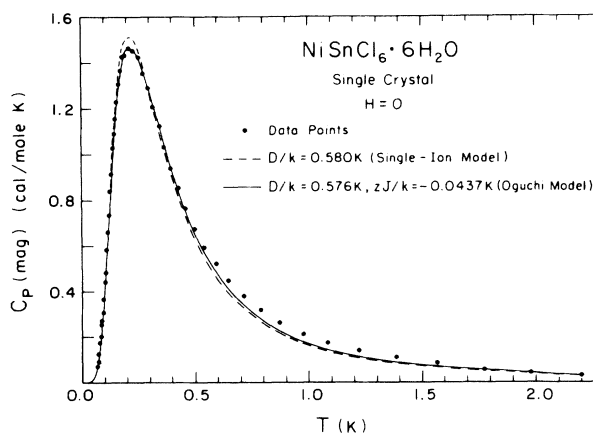

FIG. 3. Heat capacity of single-crystal specimen of NiSnCl₆·6H₂O in zero applied field corrected for lattice contributions as described in text. Dashed curve calculated for noninteracting single-ion model and solid curve with interactions treated in Oguchi approximation. Model parameters are as shown.

measured total heat capacity over the entire range from 0.06 to 4.6 K. This correction amounted to 3% of the raw values at 0.6 K, 19% at 1.2 K, and 93% at 4.6 K.

The data shown in Fig. 3 agree well with earlier results extending only down to 0.35 K. We now see a complete Schottky-like anomaly whose maximum value, 1.465 cal/mole K, is reached at $T_{max} = 0.214$ K. There is no evidence of a sharp peak indicating the onset of any kind of long-range order even at the lowest temperatures. This is consistent with our conclusion that interactions in this salt are of subcritical magnitude. This point is further emphasized by numerical evaluation of the entropy change

$$\Delta S(\text{mag}) = \int \frac{C(\text{mag})}{T} dT$$

between the limits 0.066 and 4.64 K. The result, $1.1R$, is equal to $R \ln 3$. Thus, on cooling from 4.64 to 0.066 K, all of the magnetic entropy available in the depopulation of an upper doublet and the exclusive occupation of a lower singlet for each Ni^{2+} ion has been completely removed. None is left to accommodate long-range ordering.

The dashed line in Fig. 3 is the least-squares fit of the data obtained by neglecting interactions among the Ni^{2+} ions and using Eq. (7). The fitted parameter is $D/k = +0.58$ K. Qualitatively, the fit is acceptable and clearly fixes not only the magnitude but also the sign of D. This is additional independent evidence of a singlet ground state in $NiSnCl_6 \cdot 6H_2O$. There are, however, systematic discrepancies between the measurements and the calculated curve, particularly near the maximum and on the high-temperature side. In attempting to remove these discrepancies it is reasonable to consider first possible explanations involving only the single Ni^{2+} ion. The most obvious of these would be the presence of a nonaxial (rhombic) distortion of the crystal field which could be incorporated into the spin Hamiltonian of Eq. (1) by adding a term $E(S_x^2 - S_y^2)$. For a small nonzero value of E, the upper doublet splits, causing a reduction in the maximum of the calculated Schottky anomaly as the data require. However, the best fit obtained by including a rhombic distortion is still noticeably inadequate at temperatures well above the maximum.

The only evidence of a rhombic crystal-field distortion in $NiSnCl_6 \cdot 6H_2O$ is the observation of certain weak "forbidden" transitions in the EPR spectra.[15] Given the overall trigonal symmetry of the crystal and the absence of observable magnetic anisotropy in the perpendicular plane, such behavior presumably results from the presence of small random strains in the sample. Only a small fraction of the Ni^{2+} ions need experience a significant rhombic field in order to account for the effect, and these would not noticeably affect the heat capacity of the entire system.

We consider it likely that the discrepancies evident in Fig. 3 result from the presence of subcritical interactions among Ni^{2+} ions. While it was possible to incorporate these interactions by a simple mean-field approximation in the analysis of the susceptibility data, this procedure clearly fails in the case of the zero-field heat capacity. In the absence of an applied field $\vec{H}$, the magnetization $\vec{M}$ van-

ishes and with it $\vec{H}_{eff}$, the mean field. The system behaves as N independent Ni^{2+} ions whose heat capacity is given by Eq. 7, the inadequacy of which has already been discussed. What is needed is a method of treating the effects of fluctuations or short-range order not included in the simple mean-field model. Perhaps the most elementary way of doing this is to use the Oguchi model[16] in which interactions between pairs of neighboring magnetic ions are treated exactly and the interaction of the pair with the rest of the system is approximated by a mean field. The pair, rather than the cluster consisting of an ion and all its nearest neighbors used in the Bethe-Peierls approach, is chosen for exact treatment because of its simplicity and has no structural significance. The Oguchi model usually underestimates the effects of short-range order when applied to systems exhibiting critical points. In the present instance, the fact that the interactions are of subcritical magnitude may lead to a relative insensitivity to the choice of model.

In an earlier paper[17] we have discussed the extension of Oguchi's original method for ions of spin $S = \frac{1}{2}$ to the case of a system of ions of spin $S = 1$ with uniaxial single-ion anisotropy. Considering only isotropic exchange interaction between neighboring ions, the Hamiltonian for a pair i and j becomes

$$H_{\text{pair}} = D(S_{zi}^2 + S_{zj}^2) - 2J\vec{S}_i \cdot \vec{S}_j + g\mu_B(\vec{S}_i + \vec{S}_j) \cdot \vec{H}_{eff},$$

$$(13)$$

where $S_i = S_j = 1$, $g = g_{||} = g_\perp$, and

$$\vec{H}_{eff} = \vec{H}_{app} - [2J(z-1)/Ng^2\mu_B^2]\vec{M}.$$

In this expression $\vec{M}$ is the magnetization and z the number of nearest neighbors of a given magnetic ion. The eigenvalues and eigenvectors of H_{pair} for $\vec{H}_{app} || \hat{z}$ are given in Ref. 17, as is a discussion of the calculation of the magnetization, susceptibility, and heat capacity of the Oguchi model. Since the pair ground state is a singlet and interactions are subcritical, $\vec{M}$ vanishes at all temperatures in the absence of an applied field as it does for the simple mean-field model. The zero-field heat capacity in this case is just that of $N/2$ independent pairs of exchange-coupled Ni^{2+} ions.

The solid curve in Fig. 3 is a least-squares fit of the Oguchi model to the zero-field magnetic heat capacity of $NiSnCl_6 \cdot 6H_2O$. It represents a significant improvement over the single-ion picture. Not only is the fit now quantitative up to ~ 0.5 K but some reduction of the systematic discrepancy at higher temperatures has also been achieved. The size of the residual discrepancy presumably reflects the fact that the model gives only a crude representation of short-range order in this system. The parameters of the fit are $D/k = +0.576$ K and $z|J|/k = 0.0437$ K where z is assumed to be 6 in this structure. While the zero-field heat capacity is not sensitive to the sign of J, the fitting of various in-field measurements shows J to be negative, i.e., antiferromagnetic. Again it should be noted that we have not treated magnetic dipolar coupling explicitly in our analysis, so that the interaction constant J represents the net effect of exchange and dipolar contributions.

We have fitted the Oguchi model to the $X_{||}$ and $X_\perp$ data with results which are indistinguishable from the solid curves of Fig. 2 obtained by the simple mean-field method. Again it proved necessary to allow the interactions to be anisotropic in order to remove obvious systematic discrepancies. The parameters determined in this way are $D/k = +0.59 \pm 0.02$ K, $g = 2.24 \pm 0.02$, $zJ_{||}/k = -0.066 \pm 0.003$ K, and $zJ_\perp/k = -0.033 \pm 0.003$ K. They are essentially the same as those for the simple mean-field model and agree closely with the values of D and zJ obtained by fitting the zero-field heat capacity when one notes that the weighted average of $zJ_{||}$ and $zJ_\perp$ is $-0.044k$. The consistency of these results reflects the fact that the Oguchi model has allowed us to treat approximately the effects of interionic interaction on the heat capacity as well as the susceptibility.

It is interesting to compare the parameters determined in the above analysis with values obtained from other measurements. The zero-field splitting, $D/k = +0.58$ K, is somewhat smaller than the value $D/k = +0.659$ K deduced by fitting EPR (Refs. 3 and 15) data at 4.2 K with a conventional single-ion spin Hamiltonian. As we pointed out in our preliminary report,[6] the difference appears to be significant. Oguchi, Ishikawa, and Endo[18,19] have examined theoretically the effect of exchange interaction on the energy spectrum of a system of ions with $S = 1$ and $D > 0$. They showed that in a weak external field along the unique (z) axis the system exhibits collective excitations similar to the so-called "librons" in solid orthohydrogen. It is only in large fields, $H_z \geq D/g\mu_B$, that the excitations are of the conventional magnon variety. In the weak-field case, at $T = 0$ they find that exchange interaction shifts the EPR frequency so as to yield an effective zero-field splitting $D' = D\sqrt{1 - 4zJ/D}$, where D is the splitting in the absence of coupling. It is $D = +0.576k$ which we have obtained from the analysis of our data with the mean-field models, while the single-ion analysis of the EPR results gives $D' = +0.659k$. Since $D' > D$, the above relation immediately implies that the exchange interaction is of negative sign, i.e., antiferromagnetic, as we have already concluded. It is satisfied exactly if $zJ = -0.0445k$. This is essentially the value we have obtained in our fitting of the zero-field heat-capacity data and suggests a satisfactory agreement of the collective excitation picture and observations for NiSnCl$_6$·6H$_2$O. The precise agreement is perhaps somewhat fortuitous since the coupling constants derived from our measurements have not been corrected for dipolar contributions. Agreement, in fact, is apparently poorer if the comparison is made with our value $zJ_{||} = -0.066k$ determined primarily by $X_{||}$.

Recently, Shimizu et al.[20] have extended EPR measurements on NiSnCl$_6$·6H$_2$O down to 83 mK and studied the temperature dependence of the shifts of the resonances, the linewidths, and the line shapes. They have analyzed their results using the McMillan and Opechowski[21] theory of the effect of exchange and dipolar interactions on the moments of EPR lines and their temperature dependence. Taking explicit account of the dipolar interactions, Shimizu et al. obtain good fits of their results assuming an exchange energy $zJ = -0.047k$. This agrees quantitatively with the value deduced from the collective excitation picture of the line shift and with our own result obtained by ignoring anisotropy of the interactions. In the latter procedure one apparently averages out the dipolar effects. These, however, seem to be able to account for the differences of $J_{||}$ and $J_\perp$ with the isotropic exchange constant J given by Shimizu et al. Endo and Ishikawa[22] have shown that the collective excitation picture of a system like NiSnCl$_6$·6H$_2$O yields the same results for the first and second moments of the resonance lines in the limit of large D as does the McMillan-Opechowski theory.

B. High-field behavior

In the absence of interionic interactions, a field $H_c = D/g\mu_B \cong 3800$ Oe applied along the trigonal axis should cause the lowest Zeeman component of the excited doublet of Ni^{2+} in NiSnCl$_6$·6H$_2$O to cross the singlet ground state. At this modest field the nature of the ground state changes and the system is appropriately regarded as entering the high-field regime. As mentioned in the Introduction, interionic coupling should bring about the cooperative lifting of the artificial degeneracy caused by H_c at sufficiently low temperature with the establishment of field-induced long-range spin ordering. The mean-field calculation of Tsuneto and Murao, for the case of isotropic antiferromagnetic exchange coupling ($J < 0$), predicts[5] such ordering to occur in a portion of the $H_{||}$-T plane bounded by a locus of second-order transitions which passes through the points $H_{c_1} = (D - 2z|J|)/g\mu_B$ and $H_{c_2} = (D + 4z|J|)/g\mu_B$ at $T = 0$ and $H_c' = (D - zJ)/g\mu_B$ at $T_{max} = z|J|/k$. Inserting $z|J| = 0.044k$, $g = 2.25$, and $D = 0.58k$ in these expressions, one finds the anticipated zero-temperature limits for the ordered phase to be $H_{c_1} = 3229$ Oe and $H_{c_2} = 4975$ Oe, while in a field $H_c' = 4102$ Oe ordering should occur below $T_{max} = 0.044$ K. This estimated upper temperature limit of the ordered phase is very close to the lowest temperature available with the apparatus used in the present work. However, as was suggested above, the effective interaction may be enhanced by dipolar coupling along the trigonal axis. Thus, in spite of the tendency of the mean-field approximation to overestimate transition temperatures, it was felt that T_{max} might be marginally accessible and that at least some exploratory attempts to detect field-induced spin ordering in NiSnCl$_6$·6H$_2$O should be made.

Two techniques were employed for this purpose. The first involved the observation of the temperature of an adiabatically isolated crystal as a function of increasing (or decreasing) magnetic field applied along the trigonal axis. Several series of such magnetocaloric measurements were carried out using the small crystal (3.97 g) specimen, various initial temperatures, and both increasing and decreasing fields ($0 \leq H_{||} \leq 24$ kOe). The field was varied slowly to better approximate reversible conditions and in discrete steps to increase the likelihood that the thermometer and sample were in thermal equilibrium during temperature measurements. The empirical isentrope $T_S(H)$, originating at $T(H = 0) = 148$ mK and observed in decreasing field
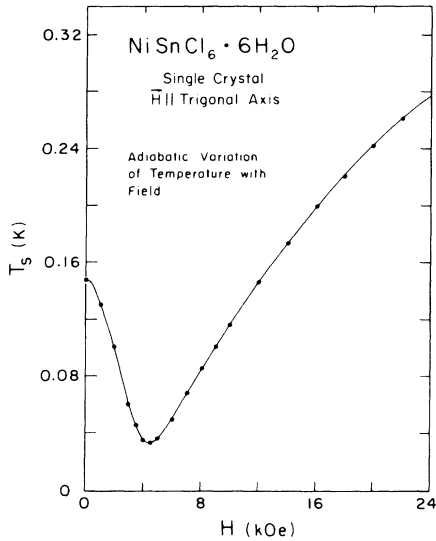
FIG. 4. Adiabatic variation of temperature of a single crystal of $NiSnCl_6 \cdot 6H_2O$ with magnetic field applied along the trigonal axis.

$H_{||}$, is shown in Fig. 4. This curve passes through a minimum at $T \cong 35$ mK, the lowest temperature reached in these experiments, without showing any obvious features indicating traversal of an ordered region. These would include distinct flattening of the minimum or the appearance of double minima. When allowance is made for the specimen demagnetizing factor, estimated from its geometry to be about 4.95, the minimum in $T_S(H)$ occurs at an internal field of ~ 4.1 kOe, which is essentially the predicted value of H_c', as expected. Curves similar to that in Fig. 4 were also obtained by increasing the field from zero starting at a temperature of ~ 150 mK. For $H < H_c'$, they demonstrate clearly that "cooling by adiabatic magnetization" can be substantial in a singlet ground-state system with very small interionic coupling.[23,24] There was no suggestion in any of our $T_S(H)$ curves that T_{max} is actually as high as or greater than 35 mK.

The second method used to search for an ordering transition in $NiSnCl_6 \cdot 6H_2O$ consisted of measuring the heat capacity $C_H(T)$ of a specimen crystal from the lowest attainable temperature with a field in the range $H_{c_1} < H_{||} < H_{c_2}$ applied along the trigonal axis. Should this initial point lie within the ordered region of the $H_{||}$-T plane then we should expect to observe a sharp cooperative anomaly in $C_H(T)$ as the phase boundary is crossed, followed at higher temperature by a rounded Schottky-like maximum. If the applied field is $\sim H_c$, then the latter anomaly should not differ very much from that associated with independent ions having a doubly degenerate ground state separated by an energy $2D$ from an excited singlet. Replacing $2D$ by $2D$ in Eq. (7), one finds for $D = 0.576k$ in that approximation $C_{max} = 0.478$ cal/mole K at a temperature $T_{max} = 0.517$ K.

Figure 5 shows the heat capacity of the 3.97-g crystal specimen measured between 0.0465 and 1.8 K with a field

$H_{||} = 4200$ Oe along the c axis. C_H exhibits a rounded Schottky-like maximum at $T_{max} \cong 0.52$ K, where $C_{max} = 0.457$ cal/mole K, passes through a minimum near 0.15 K, and is rising rapidly at the lowest accessible temperature. The temperature at which the upper rounded anomaly occurs is essentially that predicted above, ignoring interionic interactions. However, the observed value of C_{max} is less than expected on that basis by an amount ($\sim 5\%$) which appears to be significant. The solid curve in Fig. 5 has been calculated using the Oguchi model with fixed values of D/k ($= 0.576$ K), g ($= 2.24$), applied field H ($= 4200$ Oe), and a demagnetizing factor of 4.95. Only the coupling constant J was allowed to vary in the fitting process. The best fit was obtained with $zJ_{||}/k = -0.076$ K and, as is seen in Fig. 5, reproduces the data above ~ 0.3 K quite well. Unlike the fit of zero-field C_H data described above, this one is sensitive to the sign of J. The fact that the magnitude of C_H in the anomalous region is found experimentally to be less than the single-ion prediction indicates that the dominant interaction is antiferromagnetic (negative) in sign as we had previously deduced by fitting the susceptibility data.

The magnitude of $zJ_{||}$, as inferred from this fit of C_H, is in fair agreement with the value ($-0.066k$) obtained earlier from the analysis of $X_{||}$ data. The discrepancy ($\sim 13\%$) may well not be significant in view of the uncertainty involved in making the demagnetization correction. The specimen crystal was actually in the form of a parallelepiped and not an ellipsoid of revolution as was assumed in estimating the demagnetizing factor. Thus the internal field may not only differ somewhat from the value used in the calculation, it may also be slightly inhomogeneous.

The fact that C_H is still rising with falling temperature at 0.06 K without having passed through a sharp cooperative peak means, of course, that we have not observed the onset of long-range spin ordering $NiSnCl_6 \cdot 6H_2O$. This is consistent with the conclusion suggested by the magneto-
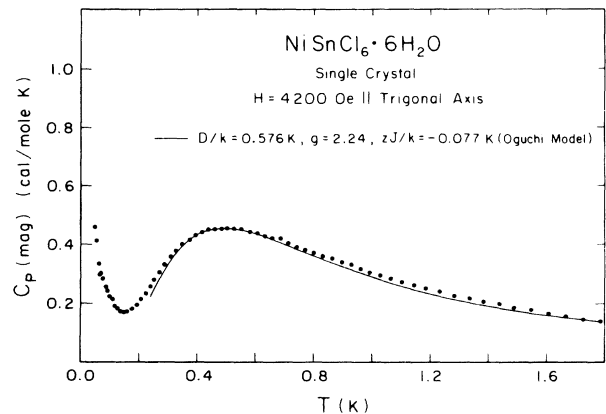

FIG. 5. Heat capacity of single-crystal specimen of $NiSnCl_6 \cdot 6H_2O$ (corrected for lattice contribution) with a field $H = 4200$ Oe applied parallel to the trigonal axis. Solid curve is calculated in the Oguchi approximation using the parameters indicated.

caloric experiments. It is tempting to suppose that we are actually observing the high-temperature "tail" of a sharp cooperative peak and that the ordering transition occurs at temperatures only slightly below our accessible range. This would probably be a safe conclusion, however, only if we knew that the applied magnetic field was perfectly aligned with the trigonal axis at each Ni^{2+} ion. The effect of field misalignment on the otherwise intersecting levels of a single Ni^{2+} is shown by dashed lines in Fig. 1(a). The perpendicular component of the field introduces matrix elements mixing the two levels and preventing the occurrence of degeneracy at H_c. The minimum energy separation Δ grows with increasing deviation from parallelism. When it is large enough relative to the interionic interaction energy, no long-range spin ordering can occur. In that case the sharp cooperative peak in the heat capacity will be replaced by a second rounded Schottky-like anomaly having roughly the features expected for two nondegenerate single-ion levels separated by an energy Δ.

Since interionic coupling is relatively weak in NiSnCl$_6$·6H$_2$O, it is particularly sensitive to field misalignment. It may be shown, for example, that if H deviates from the z direction by $\theta = 5°$, then $\Delta/k \cong 0.08$ K, which already exceeds the estimated interaction energy. Unfortunately, our apparatus did not lend itself to the correction of the field alignment in the course of an experimental run. While we estimate the accuracy of the alignment of the field and the trigonal axis of the specimen to be within $\pm 3°$ before the cryostat is closed and cooled, we cannot exclude the possibility that larger errors may actually have occurred. It is thus conceivable that even were we able to cool the specimen to much lower temperatures, an ordering transition would be unobservable as a result of misalignment. Several additional series of $C_H(T)$ measurements were carried out on a larger crystal (11.7 g) which had been worked into ellipsoidal shape to improve the accuracy of the calculated demagnetizing factor and to minimize the effect of field inhomogeneity. Applied fields of 4.4, 3.9, 3.4, and 2.9 kOe were used in these experiments. In none of them was an initial temperature less

than ~0.077 K achieved. Not surprisingly, no evidence of a phase transition was seen. The data for $H_{||} = 4.4$ kOe, for example, are similar to those in Fig. 5 already discussed. Fitting the broad Schottky-like anomaly with the Oguchi model, as before, using a calculated demagnetizing factor of 3.52 yields $zJ/k = -0.056$ K. The agreement with values of zJ deduced from other experiments is not unreasonable. It is quite possible that some of the dispersion seen in the values of zJ deduced from the high-field $C_H(T)$ data may be associated with errors of specimen alignment.

IV. CONCLUSIONS

We have obtained data on the zero-field heat capacity and single-crystal magnetic susceptibilities of NiSnCl$_6$·6H$_2$O down to temperatures as low as 60 mK thus extending considerably the range covered in earlier work. The results establish this salt as a system of Ni^{2+} ions whose $S = 1$ ground state is split into a lower singlet and upper doublet separated by $D/k = 0.576$ K with antiferromagnetic interionic interactions of subcritical magnitude. Thus no long-range spin ordering is expected or observed in zero field down to the lowest temperatures achieved. Attempts to observe the field-induced long-range ordering predicted for this system by means of the magnetocaloric effect and in-field heat-capacity measurements were unsuccessful. The ratio of the interionic coupling to D in NiSnCl$_6$·6H$_2$O is too small to permit such ordering to be seen without substantially reducing the errors of field alignment and the minimum temperature achieved in this work.

*Present address: Westinghouse Research Laboratories, Beulah Road, Pittsburgh, PA 15235.

†Present address: Hewlett Packard Co., 1501 Page Mill Rd., Palo Alto, CA 94304.

[1]L. Pauling, Z. Kristallogr. 72, 452 (1930).

[2]B. E. Myers, L. G. Polgar, and S. A. Friedberg, Phys. Rev. B 6, 3488 (1972).

[3]Y. Ajiro, S. A. Friedberg, and N. S. VanderVen, Phys. Rev. B 12, 39 (1975).

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

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

[6]S. A. Friedberg, M. Karnezos, and D. L. Meier, in Proceedings of the 14th International Conference on Low Temperature Physics, Otaniemi, Finland, edited by M. Krusius and M. Vuorio (North-Holland, Amsterdam, 1975), Vol. 3, p. 224.

[7]A. D. Algra, J. Bartolome, L. J. deJongh, C. J. O'Connor, and R. L. Carlin, Physica (Utrecht) 93B, 35 (1978).

[8]K. M. Diederix, J. P. Groen, T. O. Klaassen, J. J. Poulis, and

R. L. Carlin, Physica (Utrecht) 97B, 113 (1979).

[9]R. D. Chirico, K. O. Joung, and R. L. Carlin, J. Chem. Phys. 74, 4103 (1981).

[10]For additional details and references, see M. Karnezos, D. L. Meier, and S. A. Friedberg, Phys. Rev. B 17, 4375 (1978).

[11]M. H. L. Pryce, Proc. Phys. Soc. London, Sect. A 63, 25 (1950).

[12]See, for example, P. W. Selwood, Magnetochemistry, 2nd ed. (Interscience, New York, 1956), p. 78.

[13]R. P. Penrose and K. W. H. Stevens, Proc. Phys. Soc. London, Sect. A 63, 29 (1950).

[14]J. Owen, Proc. R. Soc. London, Ser. A 227, 183 (1955).

[15]T. How and I. Svare, Phys. Scr. 9, 40 (1974).

[16]T. Oguchi, Prog. Theor. Phys. 13, 149 (1955).

[17]M. Karnezos, D. L. Meier, and S. A. Friedberg, Phys. Rev. B 17, 4375 (1978).

[18]T. Ishikawa and T. Oguchi, J. Phys. Soc. Jpn. 31, 1588 (1971).

[19]T. Ishikawa, and Y. Endo, Prog. Theor. Phys. 55, 650 (1976).

[20]M. Shimizu, Y. Ajiro, K. Koga, and H. Abe, Solid State Commun. 26, 25 (1978); J. Phys. Soc. Jpn. 49, 170 (1980).

[21]M. McMillan and W. Opechowski, Can. J. Phys. 38, 1168 (1960); 39, 1369 (1961).

[22]Y. Endo and T. Ishikawa, J. Phys. Soc. Jpn. 42, 476 (1977).

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

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