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High-temperature series analysis of spin-one uniaxial ferromagnets: $NiMF_6 \cdot 6H_2O$ compounds

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For the first time high-temperature series for the susceptibility and heat capacity have been employed to analyze data on ferromagnetic systems with single-ion anisotropy comparable with or greater than the pair interactions between ions. The salts $NiMF_6 \cdot 6H_2O$ with $M =$ Si, Ti, Sn, Zr are spin-one ferromagnetic systems. Each has an easy-axis single-ion anisotropy and long-range dipole-dipole interaction in addition to the more commonly discussed short-range exchange interactions. We show that the same set of interaction parameters can fit simultaneously and quantitatively both susceptibility and heat-capacity data. We also discuss the unusually small deviations of the data from the mean-field predictions for the three large single-ion anisotropy systems ($M =$ Zr, Ti, Sn).

I. INTRODUCTION

The series of compounds having the formula $NiMF_6 \cdot 6H_2O$ with $M =$ Si, Ti, Sn, Zr all crystallize at room temperature in the same trigonal $NiSnCl_6 \cdot 6H_2O$ structure and can be cooled to very low temperatures preserving that structure. Interactions between Ni^{2+} ions are rather weak in these salts and of comparable strength. It has been shown by thermal and magnetic measurements[1-3] that all of them order ferromagnetically with Curie temperatures $T_c \sim 0.14-0.16$ K. In each case, there is pronounced uniaxial anisotropy with an easy axis along the crystalline trigonal axis. This anisotropy is due primarily to the single-ion mechanism. What makes the $NiMF_6 \cdot 6H_2O$ compounds of particular interest is the fact that the anisotropy energy varies with the M^{4+} ion from a value comparable with the interionic coupling in $NiSiF_6 \cdot 6H_2O$ to more than 40 times that interaction in $NiZrF_6 \cdot 6H_2O$.

The $NiSnCl_6 \cdot 6H_2O$ structure[4] belongs to the space group $R\bar{3}$. The rhombohedral unit cell contains at its center one $[Ni(H_2O)_6]^{2+}$ complex which is trigonally distorted along the trigonal axis of the crystal. In the $NiMF_6 \cdot 6H_2O$ salts, $(MF_6)^{2-}$ octahedra occupy the vertices of the unit cell. Room-temperature cell parameters range from $a = 6.26$ Å and $\alpha = 96°6'$ in the fluosilicate to $a = 6.55$ Å and $\alpha = 96°9'$ in the fluozirconate. It may be noted that the length of the cell edge, a, increases linearly with increasing radius of the M^{4+} ion in these compounds.

A trigonal distortion of the crystal field combines with spin-orbit interaction to split the $^3A_{2g}$ ground state of the $[Ni(H_2O)_6]^{2+}$ complex into a doublet ($m_s = \pm 1$) and a singlet ($m_s = 0$). In the $NiMF_6 \cdot 6H_2O$ salts the distortion is such as to leave the doublet lowest. Since interactions among the Ni^{2+} ions are weak, many of the magnetic and thermal properties of these compounds can be described reasonably well above ~ 1 K with a single-ion spin Hamiltonian of the form

$$\mathcal{H}_{\rm ion} = DS_z^2 + g\mu_B \vec{H} \cdot \vec{S} \ .$$

Here $S = 1$, the z direction coincides with the trigonal axis, the splitting factor g is nearly isotropic and equal to ~ 2.3, and $D < 0$, corresponding to the fact that the energy of the singlet exceeds that of the doublet by an amount $|D|$. The zero-field splitting parameter, D, is a measure of the single-ion anisotropy and varies between $-0.16k$ for $NiSiF_6 \cdot 6H_2O$ and $-3.1k$ for $NiZrF_6 \cdot 6H_2O$ at low temperatures. $|D|$ is found to increase linearly with the lattice parameter a and thus also with the radius of the M^{4+} ion.

At sufficiently low temperatures interactions among Ni^{2+} ions in the $NiMF_6 \cdot 6H_2O$ compounds must be included. In earlier analyses of magnetic susceptibility and heat capacity data this has usually been done only in the simple mean-field approximation which ignores fluctuation effects completely or by means of the Oguchi model[1] which incorporates then in a very restricted way. The Oguchi model treats exactly the interaction of a given paramagnetic ion with only one of its neighbors and allows these pairs to interact with the rest of the crystal via a mean field. While it exhibits a simplified kind of short-range order above T_c and in the absence of an applied field, it is essentially a mean-field model. It is not surprising, therefore, that the two kinds of analysis when appled to the $\mathrm{Ni}M\mathrm{F}_6\cdot 6\mathrm{H}_2\mathrm{O}$ ferromagnets yield estimates of coupling parameters, g-factors, and zero-field splittings $|D|$ in agreement with one another. What appears significant, however, is the fact that in some cases the mean-field method, particularly the Oguchi model, provides semiquantitative fits of many of the magnetic and thermal data over a wide range of temperature and applied field. While this suggests that some of these magnets are "mean-field-like," two features of the fitting process make this conclusion uncertain. In the first place, no attempt was made to take explicit account of magnetic dipolar interaction in these calculations. As will be demonstrated, it is not really negligible in comparison with the weak exchange coupling in these salts. Thus the fitted coupling parameters represent a mixture of exchange and dipolar interactions. Equally important is the dominance of the Curie point in the fitting process. In effect, the coupling parameters were chosen to give the observed values of T_c.

It is, therefore, desirable to reexamine the data using an improved theory—a theory which would take account of the fluctuations ignored in the mean-field treatment. We have obtained the high-temperature series expansions (HTSE) of the magnetic susceptibility along the easy axis and specific heat suitable for this group of compounds.[5] A special feature of the series expansions is that they are valid for arbitrary values of $|D|$. They also treat the magnetic dipole-dipole interactions on the same footing as the exchange interactions. These features are essential for the discussion of these compounds but bring about much complexity in the calculation. As a consequence, only four terms in each series have been found. However, similar short series have been used successfully in analyzing data for compounds with negligible single-ion anisotropies,[6,7] GdCl_3 and $\mathrm{Gd(OH)}_3$ and compounds with extreme (Ising-like) anisotropies,[8] $\mathrm{Tb(OH)}_3$. Indeed, our expectation of more conclusive findings by this approach has been borne out. The study has confirmed and elucidated the "mean-field-like" behavior of the compounds with large single-ion anisotropies. More reliable values of the parameters D, g, and J for most of the compounds have also been obtained. Furthermore, the HTSE study has demonstrated vividly the effects of the fluctuations in both the susceptibility and specific heat behavior at temperatures close to T_c.

II. HIGH-TEMPERATURE SERIES EXPANSIONS

The model Hamiltonian for the series of compounds of interest is given as follows:

$$\mathcal{H} = \mathcal{H}_{\mathrm{ex}} + \mathcal{H}_{\mathrm{dipolar}} + \mathcal{H}_{\mathrm{anisotropy}} , \tag{1}$$

where

$$\mathcal{H}_{\mathrm{ex}} = -\sum_{l,m} J_{lm} \vec{S}_l \cdot \vec{S}_m , \tag{2}$$

$$\mathcal{H}_{\mathrm{dipolar}} = \frac{1}{2} \sum_{l,m} d_{lm} \left(\vec{S}_l \cdot \vec{S}_m - \frac{3(\vec{S}_l \cdot \vec{r}_{lm})(\vec{S}_m \cdot \vec{r}_{lm})}{r_{lm}^2} \right) , \tag{3}$$

and

$$\mathcal{H}_{\mathrm{anisotropy}} = D \sum_l (S_l^z)^2 . \tag{4}$$

In the equations above, $\vec{S}_l$ denotes the spin operator on the lth lattice site, S_l^z being the z component of $\vec{S}_l$; r_{lm} is the distance from the lth site to the mth site. The summation $\sum_l$ is over all sites in the crystal lattice, while the double summation $\sum_{l,m}$ is restricted to exclude $l = m$. The parameter J_{lm} characterizes the strength of the Heisenberg exchange interaction between nearest-neighbor spins on sites l and m. The parameter characterizing the strength of the magnetic dipole-dipole interaction is d_{lm} which is given by

$$d_{lm} = (g\mu_B)^2 / r_{lm}^3 , \tag{5}$$

where the g factor is assumed to be isotropic in view of the fact that the spin-orbit coupling is much greater than the single-ion anisotropy. For $D < 0$, the system has an easy axis along the z axis. Below a critical temperature the crystal orders ferromagnetically along that axis.

The mean-field part can be separated from the above Hamiltonian and diagonalized exactly; the remaining part describing the interactions of the fluctuations can be treated in the many-body perturbation expansion. The high-temperature series expansions thus obtained allow an arbitrary value of $|D|$. In a previous paper[5] such series for the parallel susceptibility and the specific heat capacity have been obtained. The susceptibility χ is related to χ_c by the equation

$$\chi^{-1} = \chi_c^{-1} - 2[J(0) + 2E(0)] , \tag{6}$$

where

$$J(0) = \sum_m J_{lm} \quad \text{and} \quad E(0) = \sum_m E_{lm} , \tag{6a}$$

with

$$E_{lm} = -\tfrac{1}{4} d_{lm} [1 - 3(r_{lm}^z / r_{lm})^2] . \tag{7}$$

The high-temperature series for χ_c is found to be

$$\frac{\chi_c}{\chi_0} = 1 + \sum_{m,n} f(m,n)\,\sigma(m,n)\,\beta^m \ , \tag{8}$$

where

$$\chi_0 = \frac{2\beta}{2+t} \tag{8a}$$

and

$$t = e^{\beta D} \ . \tag{8b}$$

$f(m,n)$ are dimensionless functions of βD and are given in Ref. 5; $\sigma(m,n)$ are lattice sums involving the exchange and dipole-dipole interaction parameters and are also given in Ref. 5. Dropping the terms under the summation sign, so that $\chi_c = \chi_0$, Eq. (6) then gives the mean-field result for χ.

The specific-heat series at zero external field takes a similar form,

$$C_{h=0} = C_0 + k \sum_{m,n} g(m,n)\,\sigma(m,n)\,\beta^m \ , \tag{9}$$

where

$$C_0 = 2k(\beta D)^2 t(2+t)^{-2} \tag{9a}$$

and $g(m,n)$ are dimensionless functions of βD as also given in Ref. 5. The lattice sums $\sigma(m,n)$ are the same as those appearing in the expression for χ_c, Eq. (8). Again, by setting all $g(m,n)$ equal to zero, the mean-field result for $C_{h=0}$ is recovered. In both series (χ_c and C_h) the single-ion anisotropy has been treated exactly and the fluctuation corrections are incorporated in a high-temperature expansion.

Some effects of adding single-ion anisotropy and dipole-dipole interactions to the short-range Heisenberg exchange interactions in a system have been demonstrated in Ref. 5 by simple examples of cubic lattices with magnetic ordering along one of the edges of the cubic cell. Two important differences between the present case and the examples in Ref. 5 should be stressed. Firstly, the unit cell of the series $\mathrm{Ni}M\mathrm{F}_6 \cdot 6\mathrm{H}_2\mathrm{O}$ is rhombohedral rather than cubic, although the difference is not great since α is close to 90°. Secondly, the magnetic ordering is along the trigonal axis of the crystal. Consequently, the present system behaves more like a simple cubic lattice with magnetic ordering along a body diagonal than one ordering parallel to a cube edge as in Ref. 5.

An examination of the lattice sums $\sigma(m,n)$ which enter in the series expansions suggests that the magnitudes of the fluctuations can be very different for the two types of ordering. For example, when the longitudinal fluctuations dominate, as in the cases of large uniaxial single-ion anisotropy, the second-order correction to the mean-field results due to the dipole-dipole interaction is six times smaller if the spins order along the threefold body-diagonal axis rather than along a cube edge. The dipolar sums depend strongly on the direction of ordering. For a simple cubic lattice, the value of $1/N \sum [E(q)]^2/(g^2\mu_B^2/a^3)$ is 0.417 for ordering along one of the fourfold axes but is 0.071 for ordering along the

TABLE. I. Lattice sums for present system and for the simple cubic lattice. $W = (g\mu_B)^2/(a^3 J)$, a = lattice constant.

Lattice sum	Present system $\alpha = 96.13°$	Simple cubic lattice (ordering along body diagonal)
$\sigma(2,1)/J^2$	$3 + 0.0811\,W^2 + 0.3214\,W$	$3 + 0.0718\,W^2$
$\sigma(2,2)/J^2$	$1.2254\,W^2$	$1.1218\,W^2$
$\sigma(2,3)/J^2$	$6 + 0.6488\,W^2 - 1.2856\,W$	$6 + 0.5742\,W^2$
$\sigma(2,4)/J^2$	$3.4340\,W^2$	$3.6261\,W^2$
$\sigma(3,1)/J^3$	$1.9284\,W + 1.0356\,W^2 + 0.0202\,W^3$	$1.1413\,W^2 + 0.0151\,W^3$
$\sigma(3,2)/J^3$	$-15.4272\,W + 16.5696\,W^2 - 0.6463\,W^3$	$18.2615\,W^2 - 0.4848\,W^3$
$\sigma(3,3)/J^3$	$7.3598\,W^2 - 0.3017\,W^3$	$6.566\,W^2 - 0.365\,W^3$
$\sigma(3,4)/J^3$	$20.2586\,W^2 + 0.3989\,W^3$	$21.4211\,W^2 + 0.2287\,W^3$
$\sigma(3,5)/J^3$	$-3.4532\,W^3$	$-3.429\,W^3$
$\sigma(3,6)/J^3$	$40.5172\,W^2 - 1.5956\,W^3$	$42.8423\,W^2 - 0.9147\,W^3$
$\sigma(3,7)/J^3$	$4 - 1.2856\,W + 0.1377\,W^2 + 0.02856\,W^3$	$4 + 0.00918\,W^3$
$\sigma(3,8)/J^3$	$6 - 0.5163\,W^2 + 0.0097\,W^3$	$6 + 0.00344\,W^3$
$\sigma(3,9)/J^3$	$5.22\,W^2 - 0.3753\,W^3$	$6\,W^2 + 0.1297\,W^3$
$\sigma(3,10)/J^3$	$2.61\,W^2 + 0.09383\,W^3$	$3\,W^2 - 0.0324\,W^3$
$\sigma(3,11)/J^3$	$1.8388\,W^2 - 0.2358\,W^3$	$1.5\,W^2 - 0.0752\,W^3$
$\sigma(3,12)/J^3$	$1.5304\,W^3$	$1.5461\,W^3$
$E(0)/J$	$(\pi/3 - 0.1157)\,W$	$(\pi/3)\,W$

threefold axes. The corresponding value for our system is 0.081 which is quite close to the latter result. The small value of this lattice sum contributes partially to the smallness of the deviations from the mean-field values of $\chi_{\parallel}$ and C_H as will be discussed in the next section. The distortion of the real crystal from cubic symmetry also adds product terms involving both exchange and dipolar interactions. The lattice sums $\sigma(m,n)$ are essential in our later discussion so we tabulate them in Table I through the third order for the present system and for the simple cubic lattice with ordering along the body diagonal, the latter being included for purposes of comparison. Note that the rhombohedral angle α has been taken to be 96.13° in calculating the sums for the $\mathrm{Ni}M\mathrm{F}_6\cdot\mathrm{H_2O}$ structure. This is a good approximation for all four materials treated in this paper.

III. DATA ANALYSIS AND RESULTS

The susceptibility data obtained above T_c along the trigonal axes of the four isomorphous ferromagnets $\mathrm{Ni}M\mathrm{F}_6\cdot 6\mathrm{H_2O}$ (where M = Si, Sn, Ti, Zr) were fitted using the first four terms of the high-temperature series expansion of χ_c. The following expression was minimized in each case:

$$X^2=\sum\frac{(\chi_\infty-\chi_{\mathrm{HTSE}})^2}{\sigma^2}\ , \tag{10}$$

where

$$\sigma^2=(\chi_\infty/\chi_{\mathrm{expt}})^4(\sigma_{\mathrm{ind}}^2+\chi_{\mathrm{expt}}^2\sigma_N^2) \tag{10a}$$

and

$$\chi_\infty=\chi_{\mathrm{expt}}/(1-N\chi_{\mathrm{expt}}) \tag{10b}$$

$$\chi_{\mathrm{HTSE}}=\chi_c/\{1-2[J(0)+2E(0)]\}\ . \tag{10c}$$

In these equations χ_{expt} is the measured susceptibility, χ_∞ the susceptibility corrected to infinite needle geometry, N the demagnetizing factor, σ_{ind} the uncertainty in the measurement of the mutual inductance used to determine χ_{expt}, and σ_N the uncertainty in the estimate of N. σ_{ind} and σ_N represent what are considered to be the principal random errors in the data. The fitted parameters were J, the nearest-neighbor exchange integral, D, the zero-field splitting of the $S=1$ ground state (anisotropy parameter) and g, the spectroscopic splitting factor. The number of nearest neighbors z was assumed to be 6.

The lattice parameters a and α were assumed to have the values obtained by x-ray measurements at room temperature.[1-3] It was necessary to do so because of the lack of low-temperature lattice-constant data. As a result, an error of unknown magnitude will be introduced into the calculated dipolar interaction. In order to get some idea of the size of this error, it is useful to consider the results of thermal expansion measurements[9] on crystalline $\mathrm{La_2Mg_3(NO_3)_{12}\cdot 24H_2O}$ and $\mathrm{Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O}$ between 10 and 300 K. Like the $\mathrm{Ni}M\mathrm{F}_6\cdot 6\mathrm{H_2O}$ salts, these crystals belong to the space group $R\bar{3}$. The fractional changes in the lattice parameters of the hexagonal unit cell on cooling from 300 to 10 K are found to be $\Delta c/c \sim -0.016$ and $\Delta a/a \sim -0.003$. While the $\mathrm{Ni}M\mathrm{F}_y\cdot 6\mathrm{H_2O}$ salts are structurally less anisotropic than these crystals, one may suppose that contraction in this range of magnitude occurs on cooling. This would produce changes in the dipolar interaction energies of from 1 to 5%. Compared with other uncertainties in the analysis, this is probably not a serious error.

A grid search method was used to locate the minimum of X^2 in the (J,D,g) space. The truncated high-temperature series expansion is not expected to be valid close to T_c so that a somewhat arbitrary choice of the lower limit of the temperature range in which the data are fitted has been made. That limit was set at the temperature below which the data begin consistently to deviate from the fitted curve by more than one reduced $X_\nu^2=X^2/\nu$, where ν, the number of degrees of freedom, is the number of data points minus the number of parameters (3).

The same values of σ_{ind} and σ_N were used for all four salts. From the estimated precision limits on the measurement of mutual inductance we have chosen $\sigma_{\mathrm{ind}}=\pm 0.0024$. This value could be low but probably not by more than a factor of 2. σ_N is perhaps even more elusive since the specimen crystals were worked into elliposoidal form by hand and are somewhat irregular. A comparison of the demagnetizing factors calculated for several crystals from the measured principal axes and those obtained from the inverse susceptibility measured below T_c led us to choose $\sigma_N=\pm 0.005$. It should be noted that σ_N contributes very little to σ^2 above about 2 K. With σ_{ind} and σ_N as chosen, data taken over the whole temperature range being fitted contribute equally to X^2. The arbitrariness in the choices of σ_{ind} and σ_N as well as of the range covered by the data should be reflected to some extent in the values obtained for J, D, and g. However, the values of the fitted parameters were found in practice to be rather insensitive to variation in all three choices.

Figures 1 through 4 show the $\chi_{\parallel}$ and $1/\chi_{\parallel}$ vs T data between 0.4 and 4.2 K for each of the salts in the series. 0.4 K represents the lowest temperature to which data on $\mathrm{NiSiF_6\cdot 6H_2O}$ and $\mathrm{NiTiF_6\cdot 6H_2O}$ were fitted. For $\mathrm{NiSnF_6\cdot 6H_2O}$ and $\mathrm{NiZrF_6\cdot 6H_2O}$, data down to ~0.2 K were included in the fitting process. Vertical bars on $\chi_{\parallel}$ vs T plots indicate the limits of uncertainty set by σ_N as chosen above. Plots of $1/\chi_{\parallel}$ vs T bring out more clearly discrepancies between the data and the best-fitted curves at the upper end of the temperature range where $\chi_{\parallel}$ is quite small. The largest systematic differences appear above 2 K in the

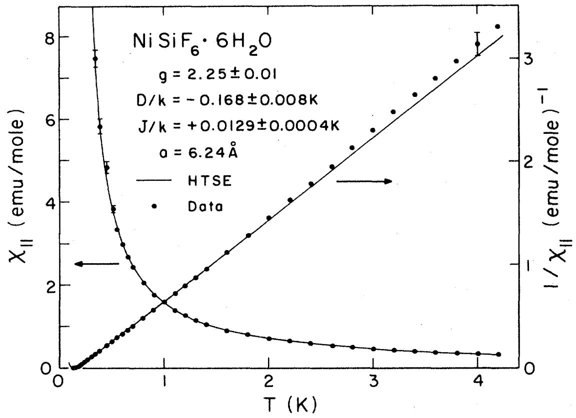

FIG. 1. Magnetic susceptibility of $NiSiF_6\cdot 6H_2O$ along the trigonal axis, $\chi_{\parallel}$ (left-hand ordinate), and its reciprocal, $1/\chi_{\parallel}$ (right-hand ordinate) as functions of the temperature above $T_c=0.135$ K.

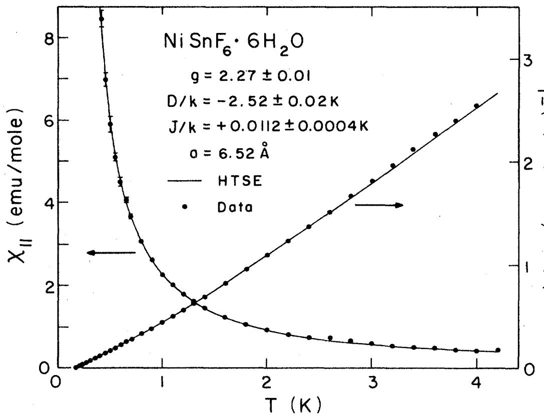

FIG. 3. $\chi_{\parallel}$ and $1/\chi_{\parallel}$ for $NiSnF_6\cdot 6H_2O$ as functions of the temperature above $T_c=0.164$ K.

case of $NiSiF_6\cdot 6H_2O$. Even here, however, the discrepancy probably does not exceed reasonable estimates of the uncertainty in the data (indicated by a vertical bar).

Table II summarizes the fitted values of the parameters g, D/k, and J/k obtained by the HTSE method and the lattice parameter a used in calculating the lattice sums for each of the four salts. The uncertainty limits shown are those set by the quality of the fit and are not necessarily measures of the accuracy of these numbers. Also shown are the corresponding values of g, D/k, and J^*/k obtained by fitting the same data together with the $\chi_{\perp}$ values using the Oguchi variant on the simple mean-field model. In this process no explicit account was taken of the magnetic dipolar interaction. Thus the fitted value of J^*/k mixes the effects of the exchange and dipolar interaction and must be regarded as an effective coupling parameter. It should be noted that values of g and D determined in the two analyses agree closely with one another and with values obtained in EPR measurements[10,11] except for the fluotitanate where small discrepancies occur. In this case, it is actually the Oguchi results which appear to be closer to the EPR values.[11] We also found that the fit of the HTSE at the lowest temperatures was poorer in this case than in the others (see Fig. 2). It is perhaps significant that the fluotitanate is the one member of this series of salts in which lattice instability has been demonstrated.[2] It is conceivable either that the specimen used in these measurements did not consist entirely of the quenched high-temperature-stable trigonal phase or that it was in a strained state. Measurements of $\chi_{\perp}$, also included in the fitting of the Oguchi model, were performed on a different crystal so that systematic errors in the $\chi_{\parallel}$ data would not necessarily

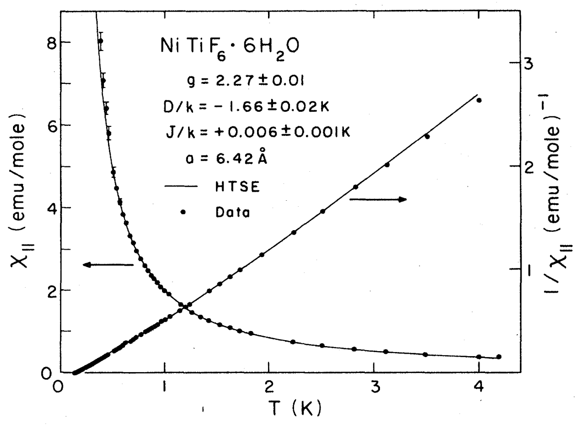

FIG. 2. $\chi_{\parallel}$ and $1/\chi_{\parallel}$ for $NiTiF_6\cdot 6H_2O$ as functions of the temperature above $T_c=0.14$ K.

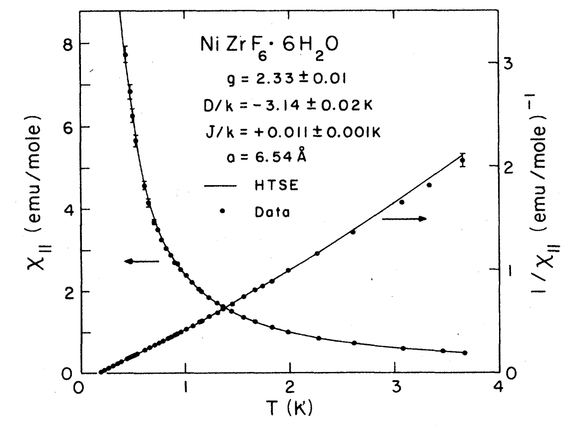

FIG. 4. $\chi_{\parallel}$ and $1/\chi_{\parallel}$ for $NiZrF_6\cdot 6H_2O$ as functions of the temperature above $T_c=0.164$ K.

TABLE II. Summary of g, D, and J parameters for $\mathrm{Ni}M\mathrm{F_6\cdot 6H_2O}$ compounds determined by fitting (a) high-temperature series expansion (HTSE) to $\chi_\parallel$ data and (b) Oguchi model to $\chi_\parallel$ and $\chi_\perp$ data. J^* is an effective coupling constant before correction for dipolar interaction (see text).

		HTSE			Oguchi model			
	a (Å)	g	D/k (K)	J/k (K)	g	D/k (K)	J^*/k (K)	J/k (K)
$\mathrm{NiSiF_6\cdot 6H_2O}$	6.26	2.25 ± 0.01	−0.168 ± 0.008	+0.0129 ± 0.0004	2.24	−0.16	0.013	0.009
$\mathrm{NiTiF_6\cdot 6H_2O}$	6.42	2.27 ± 0.01	−1.66 ± 0.02	+0.006 ± 0.001	2.26	−1.83	0.011	0.007
$\mathrm{NiSnF_6\cdot 6H_2O}$	6.52	2.27 ± 0.01	−2.52 ± 0.02	+0.0112 ± 0.0004	2.26	−2.55	0.014	0.010
$\mathrm{NiZrF_6\cdot 6H_2O}$	6.55	2.33 ± 0.01	−3.14 ± 0.02	+0.011 ± 0.001	2.33	−3.00	0.014	0.010

be as noticeable as they might be in the HTSE analysis of $\chi_\parallel$ alone. For this reason, we do not give the HTSE parameters for the fluotitanate as much weight as those for the other three salts.

As has been previously pointed out, the Oguchi model actually provides a quite reasonable fit of the susceptibility data on these salts. It is, however, obvious that the values of J estimated using the Oguchi method tend to be too low. To see this, the value of J^* given by the Oguchi model as listed in Table II is reduced by $(2/z)E(0)$, where $E(0) = (\pi/3 - 0.1157)g^2\mu_B^2/a^3$, to account for the effective field due to the dipolar interaction. Note that $-0.1157g^2\mu_B^2/a^3$ is the contribution of dipoles inside the Lorentz sphere and that the demagnetizing factor is zero for the needle shape geometry to which all data have been reduced. The corrected values of J are given in the last column of Table II.

For $\mathrm{NiSiF_6\cdot 6H_2O}$ where the single-ion anisotropy is of the same order as the effective field, the Oguchi value of J is 30% too low compared with the value estimated by the HTSE. On the other hand for the other three compounds where the single-ion anisotropy is one order of magnitude greater than the effective field, the Oguchi value of J is much closer but, except for the fluotitanate, is still a few percent too low. As has been noted, the fluotitanate may represent a special case. Given the large uncertainty limits it is probably not possible to conclude that the Oguchi and HTSE values of J are significantly different in this instance or that they are really much smaller than the J's for the other members of the series all of which are quite close to one another. The underestimation of the J values in the other salts can be traced to the fact mentioned above that in fitting the Oguchi model over a wide temperature range in the previous work, too much weight has probably been placed on data points close to the Curie temperature. It is also apparent that, except in the case of the fluosilicate, the large uniaxial single-ion anisotropy in these compounds has substantially suppressed the fluctuations.

Numerous discussions of fluctuations in the presence of dipolar interactions exist in the literature. The critical phenomena of a uniaxial system with dipolar coupling have been shown to be quasiclassical.[12] On the other hand the mean-field approximation could be extremely poor in dealing with dipolar interactions despite the fact that they are long range in nature.[13,14] The complication lies in the directional dependence of the dipolar interactions. It has been observed[13] that in certain dipolar-interacting systems the predicted value of the critical temperature in the mean-field approximation can be off by a factor of two from the experimentally measured value.

In the present series of compounds, except for the fluosilicate, the single-ion anisotropy is at least one order of magnitude greater than the pair interaction between ions. The transverse fluctuations are effectively suppressed leading to Ising-like behavior. An inspection of the longitudinal fluctuation terms shows that in second order the contribution is about one-half what it would be if there were nearest-neighbor exchange interaction alone. This reduction in fluctuation would also be observed in a simple cubic lattice with ordering (or applied magnetic field) along the body-diagonal axis. In that case the cross-product term involving both the exchange and the dipolar interactions vanishes identically by symmetry. The fluctuations are reduced by 37% assuming the same fractions of dipolar and exchange interactions in the present series of compounds, i.e., $W \simeq 1$ in the notation of Ref. 5. In the crystals under discussion the trigonal distortion adds a negative product term which brings the total reduction of fluctuations to 50%. We therefore expect to see approximately one-half of the deviation from the mean-field prediction which normally would be expected in an Ising spin-$\frac{1}{2}$ system with only nearest-neighbor exchange interactions. The fluosilicate is an exception in this series. The single-ion anisotropy is not great enough to suppress much of the transverse fluctuation. With the dipolar interaction present many more fluctuation terms appear than expected for the same system with

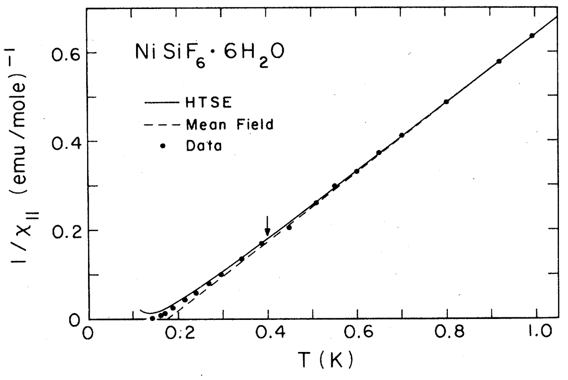

FIG. 5. $1/\chi_{\parallel}$ vs T for $NiSiF_6 \cdot 6H_2O$ below 1 K on an expanded scale.

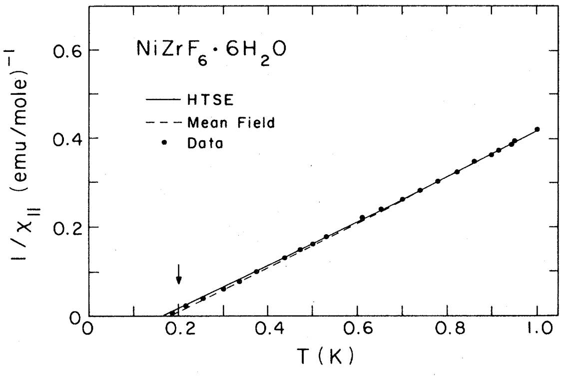

FIG. 6. $1/\chi_{\parallel}$ vs T for $NiZrF_6 \cdot 6H_2O$ below 1 K on an expanded scale.

pure exchange interaction. While being suppressed to a certain extent by the single-ion anisotropy, the transverse fluctuations are still significant.

This is brought out explicitly in Figs. 5 and 6 where $1/\chi_{\parallel}$ vs T is shown for the fluosilicate and the fluozirconate on expanded plots which include only data taken below 1 K. The full fitted HTSE is indicated in each case by a solid line, a vertical arrow marking the lower limit of the temperature range included in the fitting process. The dashed curve in each figure represents only those parts of the fitted HTSE expression corresponding to the mean-field and single-ion zero-field splitting contributions, i.e., all but the fluctuation terms.

In the case of $NiSiF_6 \cdot 6H_2O$ (see Fig. 5) the separation of HTSE and mean-field curves is significant. The fluctuation contributions to the HTSE are needed to give a quantitative fit of the data. For the fluozirconate, in which $|D|/k$ is an order of magnitude larger than in the fluosilicate, most of the transverse fluctuations are suppressed. As discussed above, Fig. 6 shows that mean-field and full HTSE curves are much closer than would be expected for a pure short-range interaction model.

Let us consider now the use of the HTSE for the heat capacity in zero field in describing the data available on $NiZrF_6 \cdot 6H_2O$ and $NiSiF_6 \cdot 6H_2O$. In the fluozirconate $|D|/k >> zJ/k$ and $C_{H=0}$ vs T exhibits both a well-resolved Schottky anomaly near $T_{\max} \sim |D|/2k$ and a sharp cooperative λ peak at T_c. In Fig. 7 we show the data together with a solid curve computed with the HTSE using the values of the parameters determined by fitting $\chi_{\parallel}$ as described above. The agreement with the observations down to ~0.2 K is really quite striking. Most impressive is the success of the theory in reproducing the small but significant short-range order "tail" on the λ anomaly just above T_c. The zero-field heat capacity in this region is a more sensitive indicator of fluctuation effects than is the susceptibility whose measurement inevitably involves the perturbing influence of an applied magnetic field.

Also shown in Fig. 7 (dashed curved) for purposes of comparison is the curve previously computed with the Oguchi model. In this case, data below as well as above T_c are surprisingly well reproduced. The HTSE and Oguchi calculations essentially agree in their representation of the Schottky anomaly. However, since it only crudely incorporates short-range order effects, the Oguchi model fails noticeably in comparison with the HTSE as T approaches T_c from above.

Unlike the other three members of our series of salts, $NiSiF_6 \cdot 6H_2O$ has a single-ion anisotropy D/k comparable in magnitude with the exchange energy zJ/k. As a result, the heat capacity exhibits only a single anomaly at low temperatures, a λ peak at T_c.

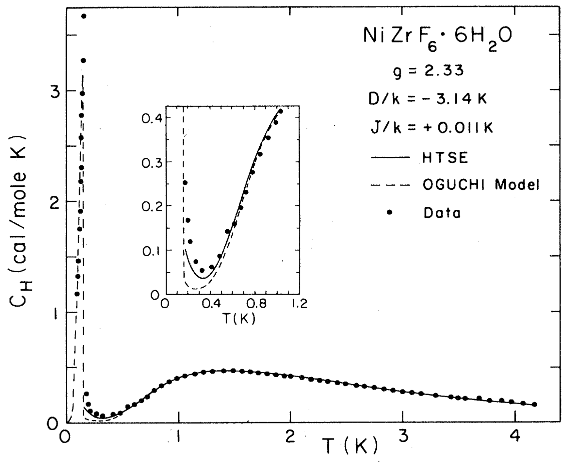

FIG. 7. Magnetic heat capacity $C_H(H=0)$ of $NiZrF_6 \cdot 6H_2O$ as a function of temperature. Data have been corrected for the lattice contribution (see Ref. 1). Oguchi model was independently fitted to the data giving $D/k = -3.14$ K and $J^*/k = 0.014$ K.

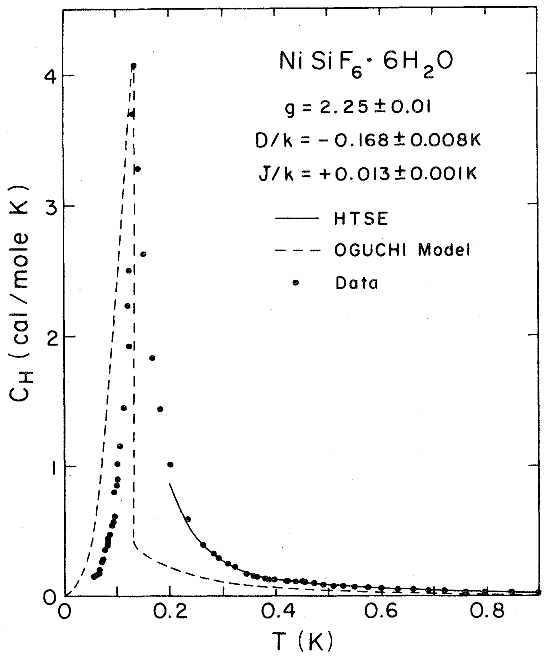

FIG. 8. Magnetic heat capacity $C_H(H=0)$ of $NiSiF_6 \cdot 6H_2O$ as a function of temperature. Data have been corrected for the lattice contribution (see Ref. 3). Oguchi model was independently fitted to the data giving $D/k=-0.16$ K and $J^*/k=0.015$ K.

Using the same set of parameters determined from the $\chi_{\parallel}$ data, quantitive agreement between the HTSE prediction and the experimental data is obtained for temperatures down to ~0.3 K as shown in Fig. 8. Also shown in the figure is a previous fit using the Oguchi model, the parameters of which are: $D=-0.16k$ and $J=0.013k$. Again, as in the case of the fluozirconate, the Oguchi model fails to pick up enough correlations to bring the curve up to meet the experimental data as T_c is approached from above.

To summarize, we have, for the first time, analyzed a series of compounds with single-ion anisotropy comparable with or greater than the pair interactions of the paramagnetic ions by employing high-temperature series. Similar analysis can be performed on other anisotropic systems, for example, rare-earth compounds for which the strength of the crystal-field potential is of the same order of magnitude as the exchange interactions. While in the present analysis, because of the complexity of the systems, only four terms in the series have been used, the reliability of the results is substantiated by the fact that the same set of parameters can simultaneously provide quantitative fits for both susceptibility and heat-capacity data. Sources of the unusually small deviations of the data from the mean-field predictions, even at temperatures quite close to T_c, have been discussed for the three compounds with large single-ion anisotropy. We also conclude that the accuracy of the mean-field approximation in the presence of dipolar interactions depends on various factors among which, the single-ion anisotropy and the direction of magnetic ordering are the essential ones.

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