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Magnetic order in three rare-earth elpasolite compounds Cs_2NaRCl_6

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The apparently undistorted fcc rare-earth salts $Cs_2NaDyCl_6$ and $Cs_2NaErCl_6$ display susceptibilities characteristic of dipolar ferromagnetism in the ordered state. This agrees with the predictions of both classical and quantum-mechanical spin-wave theories. We do not observe a predicted quantum-mechanical anisotropy due to zero-point motion of the spins. $Cs_2NaGdCl_6$ behaves in a manner consistent with a slight tetragonal distortion of its lattice, with a crystal containing many tetragonal domains oriented randomly along the fourfold axes of the cubic phase, and exhibiting anisotropic dipolar ferromagnetic order.

I. INTRODUCTION

Magnetic order due to the dipolar force is of continued interest in the study of magnetism, because the dipolar Hamiltonian is known exactly. A critical comparison between theory and experiment is possible if other interactions are negligible. Because of the anisotropy and long-range nature of the dipole interaction, theories generally have tried only to predict the most stable type of order to be expected, based on a calculation of the interaction energy of possible ordered arrays of dipoles at zero temperature. Luttinger and Tisza treat the magnetic spins as classical quantities.[1] Subsequent generalizations[2-4] of their theory treat the spins quantum mechanically, with qualitatively similar results. Another approach is the quantum-mechanical spin-wave approximation technique due to Cohen and Keffer.[5]

The type of order predicted by these theories depends in the most general case on the symmetry of the lattice in which the magnetic ions are placed, and upon the anisotropy of their moments, or g tensor. In the special case of primitive cubic symmetry, these theories all make identical predictions, which are independent of the details of particular materials. Simple cubic systems are found to be invariably antiferromagnetic, while (assuming samples are free to form domains) bcc and fcc systems are predicted always to be ferromagnets, regardless of the magnetic ion involved. Because these predictions depend only on symmetry, they are particularly important to test. Among cubic materials, results have been reported only for nuclear dipolar systems with simple-cubic symmetry,[6,7] measured in the rotating frame of reference, and for one electronic system with fcc symmetry.[8]

In this paper we present a study of the magnetic order found in several rare earth (R) elpasolite salts, Cs_2NaRCl_6. These materials were synthesized by Morss *et al.*[9] in 1970. At room temperature, they are fcc [space group $Fm3m$ (O_h^5)], with perfect octahedral point symmetry at the rare earth site. The lattice constant is large, about 10.8 Å, with about 7 Å separating the magnetic rare earth ions. The path between these is of the form R-Cl-Na-Cl-R, and bonding is primarily ionic, so the exchange interaction between rare earths should be small relative to the dipole force. This was observed in a susceptibility study of the related Rb_2NaRF_6 series.[10] Most, if not all, of the Cs_2NaRCl_6 salts containing the lighter rare earths undergo a crystalline phase transition below room temperature, and distort typically to tetragonal symmetry.[11-17] Fortunately, several of the compounds containing heavier lanthanides appear to retain cubic symmetry to low temperature. Among these are the rare earths with largest moments and highest magnetic ordering temperatures, providing particularly accessible systems to study.

II. EXPERIMENT

Single crystals of Cs_2NaRCl_6 for $R =$ Dy, Er, and Gd were grown by the Bridgman technique. The magnetically ordered ground state was determined from the dc susceptibility. For these measurements, single crystal samples were cut to an ellipsoidal shape, with the long axis oriented along (111) or (100), as determined by x-ray diffraction. A large body of data from other dipolar ferromagnets indicates that hysteresis in the ordered state is negligible.[18] When an external field is applied parallel to the magnetization axis, domain walls move so that the demagnetizing field just balances the externally applied field. The internal field $H_{\text{int}} = H_{\text{ext}} - DM$ is then equal to zero. The apparent susceptibility per unit volume in the ordered state is thus $M/H_{\text{ext}} = 1/D$, where D is the sample demagnetizing factor. Dipolar antiferromagnetic order is typically characterized by a peak in the susceptibility in the vicinity of T_c, whose magnitude is well short of $1/D$, followed by a decline at lower temperatures.

Samples were cooled inside the mixing chamber of a dilution refrigerator, in trapped fields of 0.5 and 0.05 mT. DC susceptibilities were measured using fluxgate magnetometers.[19] All of these compounds were measured in powdered form as well, to provide better thermal contact and a more accurate determination of T_c. Temperature was measured with a powdered CMN thermometer, also inside the mixing chamber, in close proximity to the samples. It was calibrated against the superconducting transitions of In, Al, Zn, Cd, $AuIn_2$, and Ir.

III. DATA AND ANALYSIS

A. $Cs_2NaDyCl_6$ and $Cs_2NaErCl_6$

Optical absorption and emission measurements on these compounds are consistent with the retention of cubic symmetry down to at least 10 K (to 4.2 K in the case of Er^{3+}).[17,20] We have obtained x-ray powder diffraction spectra down to 10 K on these materials, and single-crystal magnetization measurements of $Cs_2NaDyCl_6$ along three mutually orthogonal axes from 1 to 4 K, which also showed no observable deviation from cubic symmetry.

The susceptibility per unit volume below 1 K for $Cs_2NaDyCl_6$ and $Cs_2NaErCl_6$ is shown in Figs. 1 and 2. Both follow a Curie-Weiss law above approximately 0.5 K, and both display a kink in the susceptibility below 0.1 K, below which there is very little further change. In the case of $Cs_2NaDyCl_6$, thermal contact to single crystal samples became poor below ~20 mK, and so powdered samples were investigated as well. From the kink in the powdered sample data, we infer a magnetic ordering temperature of ~21 mK for $Cs_2NaDyCl_6$. Below T_c, the temperature independent susceptibility per unit volume of the single crystal sample (Fig. 1) is equal to 0.312, very close to the calculated value of $1/D$ for this sample, 0.308. We conclude that the order is ferromagnetic, as predicted by theory. The susceptibility of a spherical sample of $Cs_2NaErCl_6$ is qualitatively similar, but with a much higher ferromagnetic transition at ~50 mK. The limiting susceptibility of this material is 0.217, close to the calculated $D^{-1}=(4\pi/3)^{-1}=0.239$. The difference is within the combined uncertainties of the magnetometer (±10%) and the demagnetizing factor (±10%).

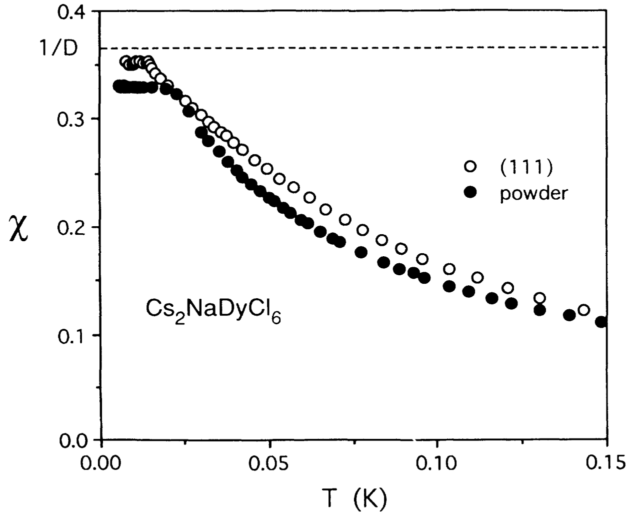

FIG. 1. DC volumetric susceptibility of single crystal (111) and powdered samples of $Cs_2NaDyCl_6$. At the lowest temperatures the single crystal susceptibility is temperature independent and very close to $1/D$, consistent with ferromagnetic order. From the kink in χ of the powder sample we infer a T_c of ~21 mK.

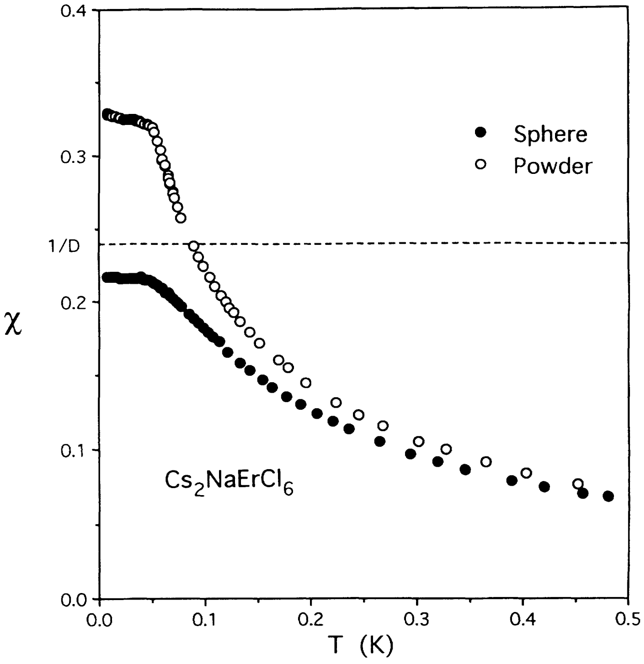

FIG. 2. DC susceptibility of single crystal (111) and powdered samples of $Cs_2NaErCl_6$. $1/D$ for the single crystal, a sphere, is indicated by the dotted line. The behavior below ~50 mK is consistent with ferromagnetism.

Above 0.2 K, a Curie-Weiss fit to the susceptibilities yields the experimental Curie constants, g factors, and Weiss constants shown in Table I. Also shown are g factors previously determined using EPR,[21,22] Curie constants predicted from these values, and Weiss constants Δ due to the dipolar interaction alone:

$$\Delta=C\left[p+\frac{4\pi}{3}-D\right] . \tag{1}$$

Here C is the Curie constant per unit volume, D is the sample demagnetizing factor, and p is a dipolar lattice summation, equal to zero for cubic symmetry. Octahedral Dy^{3+} has a doublet Γ_6 ground state, with a unique isotropic theoretical[23] g factor of $\frac{20}{3}$, rather close to that observed. Er^{3+} in this structure has been found to have a Γ_8 quartet ground state;[22] Table I shows the matrix elements P and Q, in Ayant's notation,[24] determined by EPR. The g factors associated with individual transitions in this quartet are not isotropic, but the Curie constant[25]

$$C=\frac{N_0(g_J\mu_B)^2}{2k_B}(P^2+Q^2)$$

is, since the x, y, and z axes are equivalent under O_h. In this formula, g_J is the Landé g factor. The inverse susceptibilities of both these compounds show curvature above 2 K, indicative of small crystal-field splittings between the ion's ground state and first excited state.[26] Because of this, their Weiss constants in Table I are probably not as accurate as that for $Cs_2NaGdCl_6$, described more fully in Sec. III B. The Weiss constant for

TABLE I. Measured Curie constants and derived g factors, Weiss constants, and approximate critical temperatures inferred from the susceptibility of three Cs_2NaRCl_6 salts. Spectroscopic splitting factors obtained from EPR experiments, derived Curie constants, values of the dipolar Weiss constant Δ calculated from Eq. (1), mean-field critical temperatures, and Luttinger-Tisza ground-state energies E_0 are shown for comparison.

Cs_2NaRCl_6	$R=$Dy	$R=$Er	$R=$Gd
C, cm^3 K/mol	4.1	7.0	7.2
$g_{\rm expt}$	6.6		1.91
$g_{\rm EPR}$	6.563[a]	$P=5.12$[b] $Q=1.50$	1.995[b]
$C_{\rm EPR}$, cm^3 K/mol	4.04	7.69	7.84
$\Theta_{\rm exp}$, (mK)	10 ± 20	-46 ± 40	-80 ± 40
$\Delta_{\rm calc}$, mK	20.6	96	~0
T_c, mK	21	50	35
$T_c^{\rm MF}$, mK	92	159	
E_0, mK	-45.3	-161	-22.8 to -203

[a] Reference 18.
[b] Reference 19.

$Cs_2NaDyCl_6$ agrees within experimental error with Δ calculated from Eq. (1), while that for $Cs_2NaErCl_6$ indicates an antiferromagnetic Weiss constant $\Theta_{\rm expt}=\Theta-\Delta$, due to exchange alone, of order -100 mK.

Also shown in Table I are ground-state energies calculated according to the Luttinger-Tisza theory, and mean-field critical temperatures calculated from the relation $T_c=C(p+4\pi/3)$, assuming purely dipolar interactions. For a ferromagnet, under the assumption that the crystal is free to minimize its energy by breaking into domains, the ground-state energy per spin is

$$E_0^F=-\frac{1}{2}\left[\frac{4}{3}\pi M\right](\mu_{\rm eff})=\frac{-\frac{8}{3}\pi\mu_{\rm eff}^2}{a^3}\ ,$$

where $\mu_{\rm eff}$ is the effective moment per ion and a is the lattice constant. The values in Table I were calculated from the EPR splitting factors. The magnitude of E_0 scales approximately with the observed ferromagnetic transition temperatures. The mean-field transition temperatures behave in a qualitatively similar fashion, but are several times too large.

The quantum spin-wave theory of Cohen and Keffer[5] predicts the existence of anisotropy in the ferromagnetic state due to zero point motion of the spins. In classical theories of ordering, there is no anisotropy for cubic crystals. The zero point motion prevents complete alignment of the spins, and anisotropy results from the dipolar interaction carried to second order.[27] The anisotropy energy for an fcc lattice is minimized along (111). Above T_c, it is negligible in comparison with the magnetic energy $\mathbf{H}\cdot\mathbf{M}$; below T_c it should be observable immediately for internal fields $H_i<\mathcal{E}/M\simeq0.1$ mT, where $\mathcal{E}$ is the anisotropy energy and M is magnetization. At $T=0$, the temperature independent, demagnetization limited susceptibility should be reduced from $1/D$ by a factor $\cos^2\theta$ for a single crystal, where θ is the angle between $H_{\rm ext}$ and (111). We have investigated these predictions in a single crystal sample of $Cs_2NaErCl_6$, oriented with its (100) axis parallel to the external field to produce the maximum effect ($\cos^2\theta=\frac{1}{3}$). In external field as low as 0.05 mT, and temperature as low as $0.15T_c$, we have observed no reduction in susceptibility below T_c. Within experimental error, the susceptibility below T_c was everywhere equal to $1/D$. The absence of observable anisotropy agrees with similar measurements performed on the related dipolar fcc ferromagnets $Cs_2NaR(NO_2)_6$.[8]

B. $Cs_2NaGdCl_6$

This material behaves quite differently from the preceding two. The susceptibilities of single crystal (111) and powdered samples of $Cs_2NaGdCl_6$ are shown in Figs. 3 and 4. They are very nearly identical, but unlike

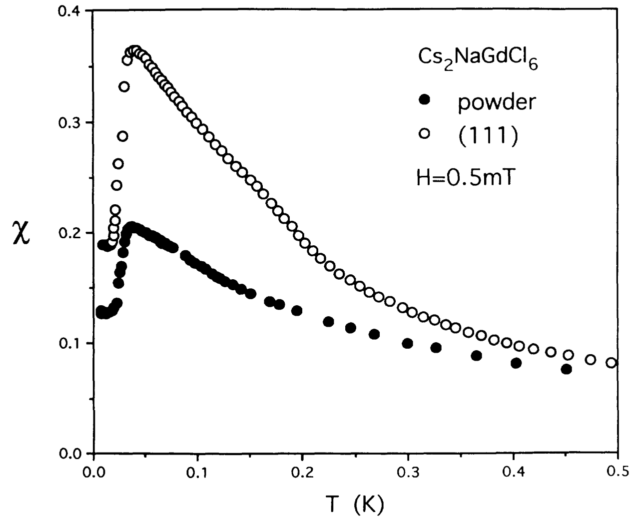

FIG. 3. Single crystal (111) and powdered sample dc susceptibilities of $Cs_2NaGdCl_6$. For the single crystal sample $D=2.26$.

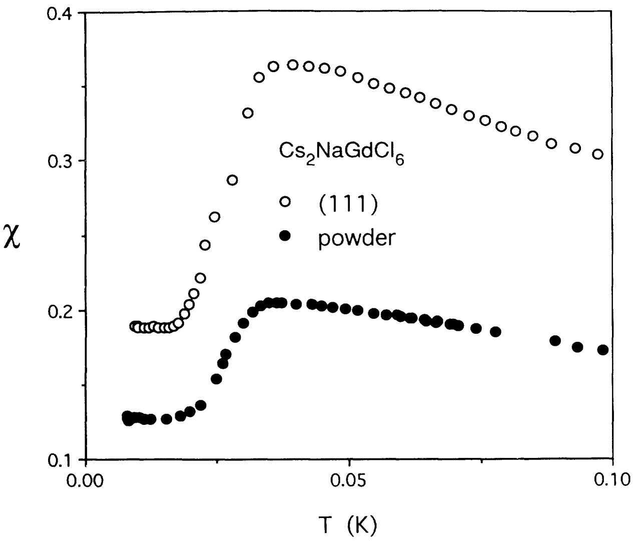

FIG. 4. An expanded view of the data of Fig. 3 from $T=0$–100 mK. The susceptibility drops rapidly below ~35 mK, and is temperature independent below ~20 mK.

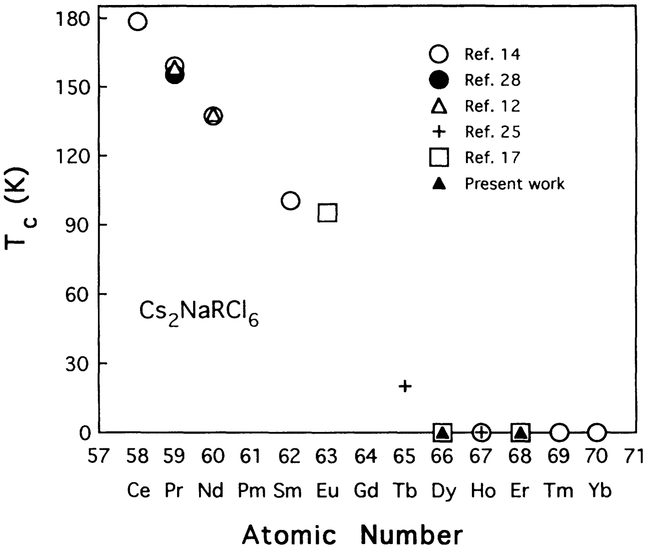

FIG. 5. Observed cubic to tetragonal lattice phase transition temperatures for the series Cs_2NaRCl_6.

$Cs_2NaDyCl_6$ and $Cs_2NaErCl_6$, both show an abrupt decrease below a peak at ~35 mK. In the powdered sample the susceptibility levels out to a temperature independent value below about 22 mK, with a magnitude equal to 0.63 of the peak value. In the single crystal sample it reaches a constant value below approximately 20 mK. The value of $\chi(T=0)$ is somewhat shape dependent in single crystal samples. It varies from 45% of the peak value when $D=1.63$ to 75 % when $D=6.62$. The value of $\chi^{-1}(T=0)-\chi_{\text{peak}}^{-1}$, which should be shape independent if the internal magnetization is uniform, is fairly consistent at 3.2 ± 0.6. Because the easy axis for dipolar ferromagnetic order in a fcc lattice is predicted to be (111),[5] the reduction in χ below T_c is presumably not due to anisotropy caused by zero point motion. Within experimental error, the susceptibility did not depend on lattice orientation in the field.

The low temperature crystalline symmetry of $Cs_2NaGdCl_6$ is not known from independent measurements. Our x-ray powder diffraction measurements at 10 K are consistent with undistorted fcc symmetry, within a precision of perhaps five parts in a thousand. There is, however, circumstantial evidence suggesting that it may not be cubic on a finer scale. Figure 5 shows the known cubic to tetragonal phase transition temperatures for a number of the Cs_2NaRCl_6 series, including those which are believed to remain cubic at ~4 K.[11–17,28]. The transition temperatures drop fairly smoothly as atomic number increases, an effect which is thought to be geometrical, due to the decreasing radius of the R^{3+} ion.[29] The immediate neighbors of Gd in the lanthanide series, Eu^{3+} and Tb^{3+}, show tetragonal distortion in this structure below 95 K (Ref. 17) and 20 K,[15] respectively. Distortion has not been observed in the compounds containing Dy^{3+} or heavier lanthanides, with the possible exception of Tm^{3+}.[15] It would therefore not be surprising if $Cs_2NaGdCl_6$ exhibited distortion at a temperature above 4 K. In the Ce, Pr, and Nd compounds, where the distortion has been studied by neutron diffraction, the lattice shows a tetragonal elongation along the c axis, decreasing in magnitude as R grows heavier. NMR and EPR measurements suggest that a crystal divides into many tetragonal domains, oriented randomly along the fourfold axes of the cubic phase.[11,14–16]

In an effort to understand the susceptibility of $Cs_2NaGdCl_6$, we have performed Luttinger-Tisza calculations of the dipolar ground-state energy of the body-centered tetragonal (bct) lattice, the Bravais lattice for a face-centered-tetragonal (fct) structure. We find that a tetragonally compressed lattice generally leads to an axial ferromagnetic ground state along the c axis, while a tetragonally elongated lattice can lead to a variety of planar magnetic structures, which depend upon the c/a ratio and the anisotropy of the magnetic ion's g factor. If we assume, as in the related hexagonal case,[30] that order occurs only along the c axis or in the a-b plane, the ground-state energy E_0 will have the general form

$$E_0=g_\perp^2E_\perp+g_\parallel^2E_\parallel \ ,$$

where $g_\perp$ and $g_\parallel$ are g factors perpendicular and parallel to the tetragonal c axis and $E_\perp$ and $E_\parallel$ are eigenvalues which depend on sublattice configuration and c/a ratio. Crossover between axial and planar order will occur when $g_\perp^2E_\perp=g_\parallel^2E_\parallel$, or

$$\left[\frac{g_\perp}{g_\parallel}\right]_{\text{crit}}^2=\tilde{g}^2=\frac{E_\parallel}{E_\perp} \ .$$

Figure 6 shows $\tilde{g}$ as a function of c/a for the bct lattice. Also shown is the type of order expected for arbitrary $g_\perp/g\|$ as a function of c/a. The Luttinger-Tisza theory predicts isotropic ferromagnetism for $c/a=1$ and $c/a=\sqrt{2}$, where $\tilde{g}=1$, corresponding to bcc and fcc symmetries. If we assume that a small tetragonal elonga-

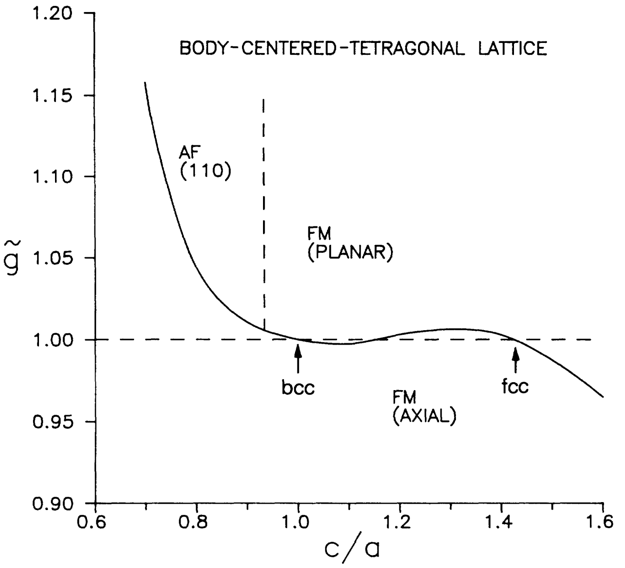

FIG. 6. Luttinger-Tisza magnetic ground states of the body-centered-tetragonal (bct) lattice, as a function of c/a and $\tilde{g}=g_{\perp}/g_{\parallel}$. The solid line denotes crossover between axial and planar order.

tion exists in $Cs_2NaGdCl_6$, as in the Ce, Pr, and Nd compounds, the classical theory predicts that this material will be either a planar or an axial ferromagnet, depending on $g_{\perp}/g_{\parallel}$.

Thus the simplest explanation of this data, namely, that $Cs_2NaGdCl_6$ is an antiferromagnet, is difficult to reconcile with theory. Alternatively, if the ordered magnetic state is ferromagnetism with anisotropy of some sort, and if this material is in fact composed of tetragonal domains, then the interpretation of the susceptibility is difficult because the samples are, in effect, polycrystalline. A qualitative explanation in this case can be given by considering the sample to be composed of dispersed, noninteracting crystalline domains, something like a dilute powder. In the axial ferromagnetic case, H_{int} will be zero below T_c along the c axis of each grain:

$$H\cos\theta - D_a M = 0\ ,$$

where θ is the angle between H and $\hat{c}$, and D_a is the axial demagnetizing factor of the grain. The susceptibility of the grain will be

$$\frac{M_z}{H}=\frac{M}{H}\cos\theta=\frac{\cos^2\theta}{D_a}\ ,$$

and the susceptibility of a large assembly of such grains, oriented orthogonally to each other along cubic axes, will be

$$\chi=\frac{1}{3}(\chi_1+\chi_2+\chi_3)$$
$$=\frac{1}{3}\frac{\gamma_1^2+\gamma_2^2+\gamma_3^2}{D_a}=\frac{1}{3D_a}\ ,$$

where the γ_i are direction cosines for the three tetragonal axes with respect to H, and D_a is a suitable average over grains. For the planar ferromagnetic case, the analogous result is $\chi=2/3D_p$, where D_p is an averaged planar demagnetizing factor of the grains. In either case, if magnetic anisotropy sets in only with magnetic order, as would be expected if the moments of the Gd^{3+} ions remain isotropic, it might be sufficient to cause a drop in the susceptibility below T_c to the values above. This reasoning is also consistent with the temperature independence of the observed susceptibility below 22 mK, or approximately $0.6T_c$ (Fig. 4). The magnetization and field within a bulk sample will be nonuniform, so these ideas are qualitative at best. If we approximate the bulk magnetization as uniform, then the experimental susceptibility is related to the internal susceptibility above by $1/\chi_{\text{expt}}=1/\chi_{\text{int}}+D$, where D is the sample demagnetizing factor, or

$$\chi_{\text{expt}}^{\text{axial}}=\frac{1}{D+3D_a}\ ,\quad \chi_{\text{expt}}^{\text{planar}}=\frac{1}{D+\frac{3}{2}D_p}\ .$$

The observed susceptibility of $Cs_2NaGdCl_6$ is qualitatively consistent with either planar or axial ferromagnetism, so that a microscopic probe such as neutron scattering or NMR will be necessary to determine the type of order with certainty.

From EPR studies of Gd^{3+} doped Cs_2NaYCl_6,[22] the crystal field ground state of the Gd^{3+} ion in an undistorted octahedral site is expected to be a Γ_6 doublet, with a unique g factor of $-\frac{14}{3}$.[23] A Γ_8 quartet with $P=-\frac{1}{2}$, $Q=-\frac{11}{6}$ lies ~36 mK above it, and a Γ_7 doublet with $g=6$ lies highest, ~86.5 mK above the ground state. Assuming the tetragonal distortion in $Cs_2NaGdCl_6$ to be quite small, and the Gd^{3+} g factors to be unchanged from these values, we obtain a Luttinger-Tisza ground-state energy of $E_0 \simeq -22.8$ mK for this salt, if the order takes place in Γ_6 alone. When compared with $T_c \simeq 35$ mK, this value is low relative to those of $Cs_2NaDyCl_6$ and $Cs_2NaErCl_6$. Because the crystal-field splittings in this material are comparable in magnitude to T_c, magnetic order may involve the excited states of the Gd^{3+} ion as well. This is similar to the case of $Cs_2NaGd(NO_2)_6$.[8] If we treat the ground and first excited states as degenerate, we obtain $E_0 \simeq -203$ mK; this is also the value for the free ion (all three states degenerate).

Well above T_c the paramagnetic susceptibility of $Cs_2NaGdCl_6$ follows a Curie-Weiss law with a measured g factor of 1.91, equal to the free ion value of 2.0 within experimental error. For single crystals of this material, we are able to obtain a more accurate value of the Weiss constant by extending susceptibility measurements up to 50 K on a Quantum Design MPMS SQUID magnetometer, since there are no complications from crystal-field splittings. We obtain $\Theta_{\text{expt}}=-80$ mK for a spherical sample, for which the dipolar Weiss constant Δ is equal to zero. In common with $Cs_2NaErCl_6$, and probably also $Cs_2NaDyCl_6$, exchange is antiferromagnetic. In these materials, therefore, exchange is not negligible. The behavior of all three salts in the ordered state is consistent, however, with an ordering process dominated by the dipolar interaction. It is possible that this is related to the fact that nearest-neighbor antiferromagnetic exchange is expected to lead to frustration in the fcc lattice.

IV. CONCLUSIONS

The apparently undistorted fcc salts $Cs_2NaDyCl_6$ and $Cs_2NaErCl_6$ behave as ideal, isotropic dipolar ferromagnets, as predicted by classical theory, within the range of our measurements. Predicted quantum-mechanical anisotropy is not observed in the ferromagnetic state, indicating that it is weaker than expected. $Cs_2NaGdCl_6$ behaves in a manner consistent with the assumption of a slight tetragonal distortion of its lattice, with a crystal containing many tetragonal domains oriented randomly along the three fourfold axes of the cubic phase. Its susceptibility is consistent with anisotropic ferromagnetic order.

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