

## Dipolar Ferromagnetic Order in a Cubic System

M. R. Roser and L. R. Corruccini

*Department of Physics, University of California, Davis, California 95616-8677*

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Classical theories and their quantum generalizations for the ordered state of a dipolar magnet make universal predictions for cubic lattices. In particular, fcc dipolar systems are predicted to be ferromagnets. We present the first direct test of this prediction, in several of the fcc  $\text{Cs}_2\text{NaR}(\text{NO}_2)_6$  rare-earth salts, and find agreement with theory. Predicted quantum anisotropy due to zero-point motion of the spins is not observed.

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The sort of magnetic order that should occur in a lattice of interacting magnetic dipoles has been studied by a number of investigators over the past half-century, beginning with the original work of Onsager<sup>1</sup> and Van Vleck.<sup>2</sup> The attraction of this problem is that the dipolar Hamiltonian is known exactly, presenting the opportunity for a critical comparison between theory and experiment. Because of the anisotropy and long-range nature of the dipolar force, most theories limit themselves to a calculation of the interaction energy of possible ordered arrays of dipoles at zero temperature. The best known of these is the theory of Luttinger and Tisza,<sup>3</sup> which treats the magnetic spins as classical quantities, and quantum extensions of this theory.<sup>4-6</sup> Cohen and Keffer<sup>7</sup> make predictions rather similar to the classical theory based on a quantum spin-wave approximation technique. In the general case, the type of magnetic order predicted by these theories depends critically on the details of the lattice parameters, and the anisotropy of the magnetic moments, or  $g$  tensor.

Universal predictions for magnetic order, independent of the details of particular systems, are made only for cubic lattices with isotropic magnetic moments. These predictions may be summarized as follows: Assuming that a ferromagnetically ordered sample is free to minimize its energy by breaking into domains,<sup>8</sup> dipolar lattices with simple-cubic symmetry will have an antiferromagnetic ground state, while bcc and fcc lattices will always be ferromagnets. These results are now over forty years old. While generally accepted, based on experimental results from systems of lower than cubic symmetry, none of these predictions has been tested directly by experiment, owing to the lack of a suitable model system. In this Letter we present the first experimental test of the last of these predictions, using the fcc rare-earth salts  $\text{Cs}_2\text{NaR}(\text{NO}_2)_6$ .

These compounds have lattice symmetry  $Fm\bar{3}$  ( $T_h^3$ ), with perfect tetrahedral  $T_h$  symmetry at the rare-earth site.<sup>9</sup> We were guided to these materials by the constraint that, in addition to having cubic symmetry, a suitable model system must separate the magnetic ions enough so that their exchange interactions are negligible

compared to the long-range dipole interaction. In these compounds, the distance between nearest magnetic ions is about  $7.8 \text{ \AA}$  ( $a \approx 11 \text{ \AA}$ ) and the path between them is of the form  $R\text{-O-N-Na-N-O-R}$ , so that exchange should be small. Rare-earth ions are dictated for the same reason. In cubic transition-metal compounds, such as the double alums, even those with the weakest interactions and lowest ordering temperatures are found to have substantial exchange.<sup>10</sup> We have synthesized most of these compounds from Ce through Yb. Powder x-ray-diffraction spectra taken at 10 K indicate that all members of the series retain their cubic symmetry down to that temperature, unlike the related series  $\text{Cs}_2\text{NaRCl}_6$ .<sup>11</sup> Samples are obtained both as fine precipitates from solution and also as single crystals grown from slowly diffusing solutions or in silica gel.<sup>12</sup> Single-crystal sizes ranged up to  $\sim 1 \text{ mm}^3$ . The shape of the crystallites is roughly spherical, showing both octahedral and cubic facets.

The magnetically ordered ground state in these crystals was determined from the dc susceptibility. Dipolar ferromagnets typically exhibit negligible hysteresis in the ordered state, and are able to maintain the internal field  $H_{\text{int}} = H_a - DM$  equal to zero in the presence of an external field  $H_a$ , applied parallel to the magnetization axis, where  $D$  is the sample demagnetizing factor. This yields a constant susceptibility per unit volume  $\chi_c = M/H_a$  equal to  $1/D$  below the ordering temperature.<sup>13</sup> In the antiferromagnetic case, the susceptibility typically rises to a maximum in the vicinity of  $T_c$ , then drops below that temperature. The maximum is usually well short of  $1/D$  in magnitude. Samples were cooled inside the mixing chamber of a dilution refrigerator, in trapped fields of 0.5 and 0.05 mT. Magnetization was measured using fluxgate magnetometers<sup>14</sup> for polycrystalline samples, and a SQUID magnetometer for single crystals. Because of the small crystallite size in the samples, thermal contact was very good and thermal time constants were short. Because these materials are cubic, and  $x$ ,  $y$ , and  $z$  axes are equivalent under  $T_h$ , their magnetic moments are isotropic and polycrystalline susceptibilities are equivalent to those of single-crystal samples.

The sample temperature was measured using a cerium magnesium nitrate (CMN) thermometer, also inside the mixing chamber in close proximity to the samples. This was calibrated against the superconducting transitions of Al, Zn, Cd, AuIn<sub>2</sub>, and Ir.

We have observed magnetic transitions in the Nd, Gd, Dy, and Er salts of this series. The others either show no order above  $\sim 6.5$  mK, or have nonmagnetic crystal-field ground states. dc susceptibility data as a function of temperature are shown in Fig. 1, for single-crystal samples of Gd and Dy oriented along (100), and polycrystalline samples of Nd and Er. All exhibit a monotonically increasing susceptibility as the temperature is lowered, and display a kink in the vicinity of the ordering temperature. Below this temperature the susceptibility is nearly constant. For single-crystal samples, the value of  $\chi_v(T=0)$  below  $T_c$  lies within about 3% of  $1/D$  calculated for a spherical sample. For the polycrystalline samples, where the demagnetizing field is presumably nonuniform,  $\chi_v(T=0)$  nevertheless lies within about 20% of this value. Single-crystal measurements for a variety of orientations show, within experimental error, that  $D\chi_v(T=0)$  is independent of orientation in the external field. For the Gd, Dy, and Er compounds, we infer that the order is ferromagnetic, in agreement with the theories of Luttinger and Tisza of Cohen and Keffer. We could not cool the Nd salt far enough below  $T_c$  to establish its ordered state with the same certainty, but the similar magnitude of its maximum susceptibility to those of the other compounds of this series argues in favor of ferromagnetism. These results contrast with the antiferromagnetic order typically seen in dilute exchange-coupled materials with fcc symmetry,<sup>10</sup> including metallic nuclear systems.<sup>15</sup> They also differ from the nuclear dipolar order observed in CaF<sub>2</sub> and related materials, in the rotating frame of reference, where the type of order

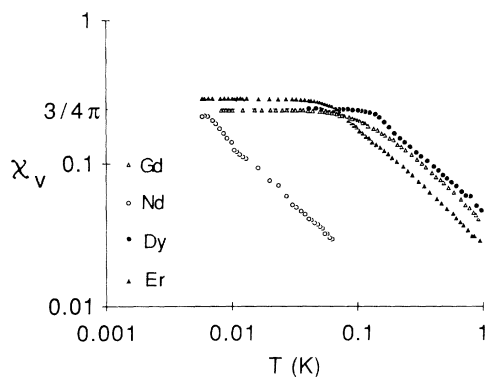


FIG. 1. dc susceptibility data as a function of temperature for single-crystal samples of Cs<sub>2</sub>NaGd(NO<sub>2</sub>)<sub>6</sub> (100) and Cs<sub>2</sub>NaDy(NO<sub>2</sub>)<sub>6</sub> (100), and polycrystalline samples of Cs<sub>2</sub>NaNd(NO<sub>2</sub>)<sub>6</sub> and Cs<sub>2</sub>NaEr(NO<sub>2</sub>)<sub>6</sub>. All exhibit a kink below which  $\chi$  is approximately constant and very close to  $1/D$  (sphere), indicating ferromagnetic order.

depends on the crystal's orientation in an external magnetic field, as well as the sign of the spin temperature.<sup>16</sup>

Crystal-field splittings in some of the Cs<sub>2</sub>NaR(NO<sub>2</sub>)<sub>6</sub> rare-earth salts are rather small, in some cases apparently of order 1 K.<sup>17</sup> Possibly because of this, the susceptibility of Cs<sub>2</sub>NaDy(NO<sub>2</sub>)<sub>6</sub> does not accurately obey a simple Curie-Weiss law above  $T_c$ . For the remaining three salts which do, an estimate of the strength of the residual exchange interaction can be obtained from measurements of the Weiss constant well above  $T_c$ . The mean-field susceptibility in this region is  $\chi = C/(T - \Delta - \theta_{ex})$ , where  $C$  is the Curie constant per unit volume,  $\theta_{ex}$  is the Weiss constant due to exchange, and  $\Delta$  is due to dipolar interactions, and, for single crystals, can be calculated as<sup>10</sup>

$$\Delta = C(p + 4\pi/3 - D).$$

In this expression  $p$  is a constant equal to a dipolar lattice summation and depends upon lattice symmetry. For cubic lattices it is identically zero. For a spherical sample of these materials ( $D = 4\pi/3$ ),  $\Delta$  is therefore predicted to be zero. We have measured the susceptibility of an approximately spherical single-crystal sample of Cs<sub>2</sub>NaGd(NO<sub>2</sub>)<sub>6</sub> in SQUID magnetometers from 0.5 to 50 K, where one expects no complication from crystal-field effects, and obtain  $\Delta + \theta_{ex}$  equal to  $-5 \pm 20$  mK. From this we conclude that  $|\theta_{ex}| \lesssim 10$  mK in magnitude, smaller in magnitude than the dipolar energy of interaction (see below) and  $T_c$  ( $\approx 45$  mK). This conclusion should apply to the other compounds of the series as well. A similar analysis of a single-crystal sample of Cs<sub>2</sub>NaEr(NO<sub>2</sub>)<sub>6</sub> from 1 to 5 K, and a polycrystalline sample of Cs<sub>2</sub>NaNd(NO<sub>2</sub>)<sub>6</sub> over the interval 50 mK  $< T < 1$  K, yields  $\Delta + \theta_{ex} = 0 \pm 30$  mK (Er) and  $-5 \pm 3$  mK (Nd), also quite small. These constants, as well as other relevant data, are listed in Table I. The magnitude of  $\theta_{ex}$  suggests that ion-ion forces are primarily dipolar, with exchange relatively unimportant. This conclusion is reinforced by a calculation (below) of the dipolar energy of ordering, which indicates that the observed ordering temperatures scale approximately as the square of the effective magnetic moment, as would be expected for dipolar interactions.

The crystal-field ground state of the different rare-earth ions can, in most cases, be determined from the Curie constant above  $T_c$ . An ion at a site of  $T_h$  symmetry experiences a crystal-field potential of the form<sup>18</sup>

$$V = B_4^0(O_4^0 - 5O_4^4) + B_6^0(O_6^0 - 21O_6^4) + B_6^2(O_6^2 - O_6^6),$$

where the  $B_n^m$  are constants and the  $O_n^m$  are Stevens operator equivalents.<sup>19</sup> Kramers ions (including all those studied here) have ground multiplets split by this interaction into three types of doublets,  $\bar{E}$ ,  $\bar{F}_1$ , and  $\bar{F}_2$ , the latter two degenerate Kramers conjugates derived from the cubic  $\Gamma_8$  quartet. For Nd<sup>3+</sup> in this structure, the susceptibility is fitted very closely by that predicted

TABLE I. Measured values of the Weiss constant ( $\Delta + \theta_{\text{ex}}$ ), inferred values of  $\theta_{\text{ex}}$ , critical temperatures inferred from the susceptibility, classical ferromagnetic ordering energies, and crystal-field ionic ground states for four  $\text{Cs}_2\text{NaR}(\text{NO}_2)_6$  rare-earth salts.

Material	$\Delta + \theta_{\text{ex}}$ (mK)	$\theta_{\text{ex}}$ (mK)	$T_c$ (mK)	$E^F$ (mK)	Probable ion ground state
$\text{Cs}_2\text{NaDy}(\text{NO}_2)_6$			$60 \pm 10$	-169	$\bar{F}_1, \bar{F}_2$
$\text{Cs}_2\text{NaEr}(\text{NO}_2)_6$	$0 \pm 30$	$0 \pm 30$	$40 \pm 5$	-124	$\bar{F}_1, \bar{F}_2$
$\text{Cs}_2\text{NaGd}(\text{NO}_2)_6$	$-5 \pm 20$	$-5 \pm 20$	$45 \pm 5$		$\bar{E}$
$\text{Cs}_2\text{NaNd}(\text{NO}_2)_6$	$-5 \pm 3$		$6.5 \pm 1$	-6.7	$\bar{E}$

for the tetrahedral doublet  $\bar{E}$ , with a unique  $g$  factor of  $\frac{8}{3}$ .<sup>17</sup> For  $\text{Er}^{3+}$ , the Curie constant per mole is equal to approximately  $6.0 \text{ cm}^3 \text{ K/mol}$ ; for  $\text{Dy}^{3+}$ , approximately  $8.2 \text{ cm}^3 \text{ K/mol}$ . This, and preliminary EPR spectra, are consistent with ground states consisting of the two degenerate doublets  $\bar{F}_1, \bar{F}_2$ .<sup>17</sup> For  $\text{Gd}^{3+}$ , the crystal-field splittings are expected to be quite small, approximately the same magnitude as the dipolar interaction energy, so the crystal-field ground state cannot be inferred from the susceptibility alone. Based upon crystal-field parameters of  $\text{Gd}^{3+}$  in other sites of cubic symmetry,<sup>20</sup> the most likely ground state is a doublet  $\bar{E}$  composed largely of the cubic  $\bar{E}_1$  ( $\Gamma_6$ ), with a  $g$  factor near  $\frac{14}{3}$ .<sup>21</sup>

Regardless of the identities of the ions' crystal-field ground states, one can, in principle, calculate the ferromagnetic energy of ordering in the Luttinger-Tisza theory. Assuming the system is free to minimize its energy by breaking into domains, the energy per spin is

$$E^F = -\frac{1}{2} \left( \frac{4}{3} \pi M \right) (\mu_{\text{eff}}) = -\frac{8}{3} \pi \mu_{\text{eff}}^2 / a^3,$$

where  $\mu_{\text{eff}}$  is the effective moment per ion and  $a$  is the lattice constant. For doublet ground states we obtain  $\mu_{\text{eff}}$  from the molar Curie constant in the mean-field limit,  $C_{\text{mol}} = N_A \mu_{\text{eff}}^2 / k_B$ . For  $\bar{F}_1, \bar{F}_2$  we estimate  $\mu_{\text{eff}}$  from the corresponding octahedral case ( $B_6^2 = 0$ ).<sup>21</sup> This yields ground-state energies  $E^F/k_B$  of approximately  $-169 \text{ mK}$  for  $\text{Cs}_2\text{NaDy}(\text{NO}_2)_6$ ,  $-124 \text{ mK}$  for  $\text{Cs}_2\text{NaEr}(\text{NO}_2)_6$ , and  $-6.7 \text{ mK}$  for  $\text{Cs}_2\text{NaNd}(\text{NO}_2)_6$ . Quantum theories of the ordering energy change these values by only a few percent. The magnitude of  $E^F$  in these salts follows the same sequence as the ordering temperatures, which are approximately  $60 \text{ mK}$  (Dy),  $40 \text{ mK}$  (Er), and  $6.5 \text{ mK}$  (Nd), respectively. Mean-field critical temperatures can be calculated from the relation  $T_c = C(p + 4\pi/3)$ , assuming purely dipolar interactions. They are roughly twice those observed.

In the case of  $\text{Cs}_2\text{NaGd}(\text{NO}_2)_6$ ,  $\mu_{\text{eff}}$  is not known, and all that can be said with certainty is that the magnitude of  $E^F/k_B$  cannot exceed the free-ion value of  $-188 \text{ mK}$ . Since the crystal-field splittings in the case of  $\text{Gd}^{3+}$  are comparable in magnitude with this range, one cannot conclude that magnetic order takes place in the ion's ground state only. If it does, and if the ground doublet is characterized by  $g = \frac{14}{3}$ , then  $E^F/k_B = -21 \text{ mK}$ . The magnitude of the ordering temperature,  $\sim 45 \text{ mK}$ , in conjunction with the results for the other ferromagnetic

salts in this series, suggests that magnetic order probably does not occur solely in the  $\text{Gd}^{3+}$  ground state. This is different from the case of  $\text{Gd}$  ethyl sulfate, another dipolar  $\text{Gd}$  system, where the properties of magnetic order can be explained by the ion's ground state alone.<sup>22</sup>

The quantum spin-wave theory of Cohen and Keffer<sup>7</sup> predicts that the ferromagnetically ordered state should display anisotropy. Classically, there exists no anisotropy energy for a cubic crystal; in a quantum theory, the spin does not commute with the dipolar Hamiltonian, and the moments display zero-point motion which prevents complete alignment. Anisotropy results from the dipolar interaction carried to the second order.<sup>8</sup> The anisotropy energy is given by

$$\mathcal{E} = (M^2/S) [K_1(a_1^2 a_2^2 + a_1^2 a_3^2 + a_2^2 a_3^2) + K_2 a_1^2 a_2^2 a_3^2],$$

where  $a_i$  are direction cosines,  $S$  is spin, and the anisotropy constants are calculated to be  $K_1 = -0.0235$ ,  $K_2 = -0.3966$  for fcc. The anisotropy energy is minimized along (111). The effects of anisotropy should be observable below  $T_c$  for internal fields  $H_i \lesssim \mathcal{E}/M \approx 0.1 \text{ mT}$ . Above  $T_c$ , we calculate the expected anisotropy to be negligible, regardless of field. Thus, in our measurements anisotropy should not be visible above  $T_c$ , but for sufficiently small fields should set in at or below  $T_c$ , producing a drop in the apparent susceptibility. At  $T=0$ , the demagnetization-limited susceptibility should be reduced from  $1/D$  by a factor of  $\cos^2 \theta$  for a single crystal, where  $\theta$  is the angle between  $H_0$  and the closest anisotropy axis. For a powder sample,  $\chi(0)$  will be reduced by  $\langle \cos^2 \theta \rangle = \frac{1}{3} + 4/3\pi = 0.7577$ , if the anisotropy axis is (111). We do not observe this reduction in either case, for external fields as small as  $0.05 \text{ mT}$ , temperatures as low as  $0.1 T_c$ , and single crystals oriented with  $H_0$  parallel to (100), where the effect should be maximal ( $\cos^2 \theta = \frac{1}{3}$ ). At temperatures this low, where one expects  $M(T)/M(0)$  to exceed  $0.95$ , both classical and quantum treatments predict anisotropy constants at least  $60\%$  of their maximum values at  $T=0$ .<sup>23</sup> In the related compound  $\text{Cs}_2\text{NaGdCl}_6$ , where anisotropy is introduced by a slight lattice distortion, we have observed precisely this effect. We conclude that either smaller applied fields are necessary to observe the quantum anisotropy, or, for unknown reasons, it is not present.

A well-known group-theoretical result states that simple ferromagnetism is not possible in a strictly cubic lat-

tice.<sup>24</sup> In exchange-coupled cubic ferromagnets, such as iron, this inconsistency is resolved by ascribing a small lattice distortion due to magnetostriction in the ordered state. If this explanation is also correct for dipolar ferromagnets, order will never be truly isotropic, because the classical theory predicts *isotropic* ferromagnetism only in the perfectly cubic case. For locally isotropic moments, an arbitrarily small distortion along one of the cubic axes results in either axial ferromagnetism, for an axial compression, or planar ferromagnetism for an elongation. The magnetostriction is estimated<sup>8</sup> to be of order  $\kappa M^2 \sim 10^{-8}$  in these materials, where  $\kappa$  is the compressibility. Because it is so small, a classical calculation indicates that magnetostriction will lead to observable anisotropy only for internal fields  $H_i \lesssim 10^{-8}$  mT, well below the limits of our observations.

In conclusion, we have confirmed long-standing predictions of ferromagnetic order in fcc dipolar systems by classical and quantum theories. These predictions appear to hold for four members of the series  $\text{Cs}_2\text{NaR}(\text{NO}_2)_6$ . The absence of quantum anisotropy in the ordered state remains to be explained.

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