Magnetic ordering in KDy_3F_{10}: A system containing three orthogonal Ising lattices

Stephen L. Chamberlain,* Gang Luo, and L. R. Corruccini
Physics Department, University of California–Davis, Davis, California 95616
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The rare-earth fluorides with KY_3F_{10} structure are cubic, with three nonequivalent sites for the rare-earth ion, each with a tetragonal symmetry axis aligned along one of the three cubic axes. We present magnetic susceptibility and magnetization results for KDy_3F_{10}, a material which displays nearly complete (Ising) anisotropy of the magnetic moments along the local symmetry axis. Magnetic exchange is antiferromagnetic, and the dipole-dipole interaction favors antiferromagnetism in the absence of exchange. Despite this, we observe a spontaneously polarized magnetic state at low temperature. The explanation appears to lie in the relative magnitudes of the two interactions.

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I. INTRODUCTION

The rare-earth compounds isomorphous with KY_3F_{10} have a novel cubic structure, containing three nonequivalent sites for the magnetic rare earth ions. The structure was first analyzed by Hong and Pierce.[1] The space group is fcc ($Fm3m$) but the symmetry of the rare-earth sites is tetragonal (C_{4v}), with the symmetry axis oriented along one of the three cubic axes. The primitive fcc unit cell is pictured in Fig. 1. The magnetic ions are separated by a minimum distance of approximately 3.9 Å, and can be pictured as occupying the vertices of a network of corner-sharing octahedra. For antiferromagnetic exchange interactions, the system is partially frustrated. In several of these compounds, containing Dy^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+}, the magnetic moments of the rare-earth ions are highly anisotropic and essentially (local) Ising spins, with the component orthogonal to the tetragonal axis in some cases too small to measure. These unique materials are thus composed of three orthogonal Ising systems. Because of the extreme anisotropy of the moments, simple uniaxial magnetic order is not possible in these systems, requiring a more complex ground state. In this paper we report the magnetic properties of the first of these compounds, KDy_3F_{10}.

Aside from their cubic structure, in certain respects these materials are similar to the tetragonal $LiYF_4$ compounds.[2] Both classes of materials have been studied for laser applications. The rare-earth point symmetry is tetragonal in both cases (S_4 in $LiYF_4$), and the rare-earth separation and density are very similar.[3] Also similar to those materials,[3] we find that in KDy_3F_{10} the magnetic exchange interaction and the dipole-dipole interaction are intrinsically the same order of magnitude. In most of the $LiYF_4$ materials, the ordered magnetic state is predicted correctly by the dipole-dipole interaction alone.[4,5] We were motivated to study the magnetic properties of these materials, which have not been reported before, first because of their very interesting structural characteristics, and also to determine whether their magnetic ground state is similarly dominated by the dipolar interaction. In contrast we find, similar to the situation in some frustrated pyrochlore systems, including "spin ice,"[6] that both interactions must be taken into account in describing KDy_3F_{10}. We show that both interactions separately favor antiferromagnetism in this material, but because of the peculiar KY_3F_{10} structure, the effect of exchange is drastically reduced, and under certain conditions the combination favors a polarized state, which we observe.

II. EXPERIMENTAL DETAILS

Samples of KDy_3F_{10} were made by combining and mixing the powders of the commercial rare earth trifluoride with

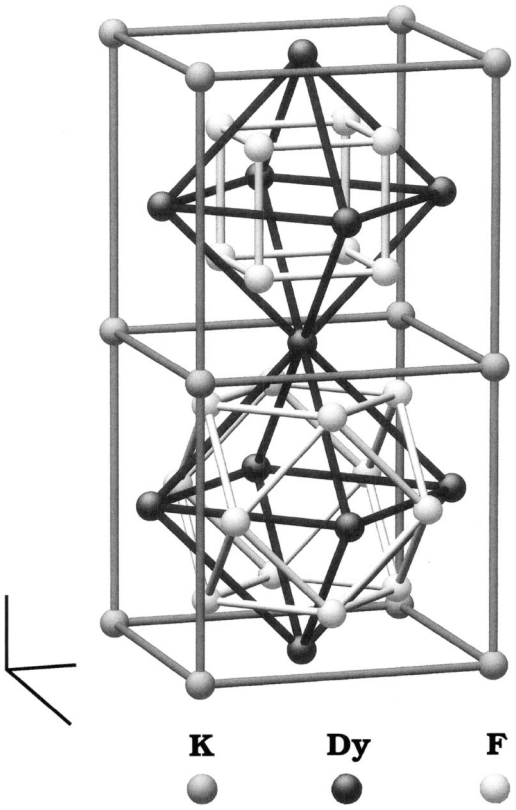

FIG. 1. The primitive fcc unit cell for the KY_3F_{10} structure. The lightest spheres represent fluorine ions, the darkest ones rare earth, and the intermediate ones potassium. The rare-earth ions occupy the vertices of a network of corner-sharing octahedra, each with C_{4v} symmetry about an axis oriented parallel to one of the cubic axes, shown at lower left.

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KF in stoichiometric ratio. The starting materials were dried by heating in vacuum at 200 °C before combining in an argon-filled glove box. To eliminate residual oxide contamination, 10% NH_4HF_2 was added to the samples, which were then heated in a Ni boat under flowing argon at 350 °C for several h. Transparent single crystals of KDy_3F_{10} were grown from the powdered samples in sealed Ni crucibles using the Bridgman technique, at a temperature slightly over 1040 °C. Subsequent chemical analysis found no detectible Ni impurities. Powder x-ray diffraction spectra of the completed samples were very clean, with all peaks indexed to the cubic KY_3F_{10} structure. The lattice constant for KDy_3F_{10} is 11.634 Å, consistent with previously reported values.[7]

Static magnetic susceptibilities were measured using shaped spherical samples with diameters of 1 to 2.5 mm. Above 1.7 K, data were obtained using a Quantum Design MPMS SQUID magnetometer, at fields of 10, 30, and 50 mT. Within experimental error, susceptibility was independent of field in this range. Below 2.5 K, samples were cooled inside the mixing chamber of a dilution refrigerator, and magnetization was measured using fluxgate magnetometers. Susceptibility measurements were taken at fields of 1, 10, and 50 mT, with the lowest field useful primarily at the lowest temperatures. Data taken with the dilution refrigerator were normalized to agree with data taken in the squid magnetometer in the range 1.7–2.5 K. Magnetization sweeps as a function of field were obtained using the same instrument. Temperature was measured using a CMN thermometer at 1 mT, and with a germanium resistance thermometer, down to 70 mK only, at 10 and 50 mT. Both were located inside the mixing chamber next to the samples. Accuracy in the temperature readings is estimated to be about 2% above 30 mK, and ± 0.6 mK below 30 mK.

III. EXPERIMENT AND DISCUSSION

The susceptibility of KDy_3F_{10} in the temperature range below 1.5 K is shown in Fig. 2. Above about 0.6 K, it obeys a Curie-Weiss law fairly accurately, with $\theta_w = -1.3 \pm 0.2$ K. There is a knee in the field cooled data in the vicinity of 0.2 K, below which the susceptibility is nearly constant at $\chi_{\max} = 7.8\ \mathrm{cm}^3/\mathrm{mol}$. The corresponding dimensionless susceptibility is $\chi_{\mathrm{mol}}/V_{\mathrm{mol}} = 0.197$, very close to the demagnetization limit for a spherical sample of $1/D = 3/4\pi = 0.239$. This is the behavior observed at low temperature in a variety of ferromagnets below T_c.[8,9] The small drop in susceptibility in the vicinity of 10 mK is possibly due to instrumental drift; it was not observed in other specimens. Zero-field cooled data are much lower below about 0.2 K, consistent with increased pinning of domain walls at lower temperature.

Within the mean-field approximation, θ_w for a spherical sample is the sum of parts due to the exchange and dipole-dipole interactions:[9] $\theta_w = \theta_w^{\mathrm{ex}} + \theta_w^{\mathrm{dip}}$, where θ_w^{dip} is given by a lattice sum.[10] Using the lattice parameters appropriate for KY_3F_{10}, we obtain the general result for this structure to be

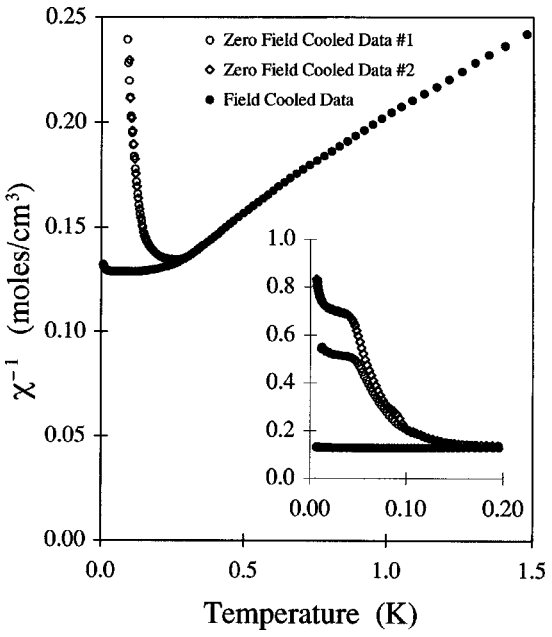

FIG. 2. Inverse susceptibility of KDy_3F_{10} from 0 to 1.5 K. The results of two sets of zero-field cooled measurements and one set of field cooled measurements are shown. Below 0.2 K, the FC data are nearly constant and very close to the demagnetization limit, consistent with a spontaneous magnetization. The insert displays the full range of data below 0.2 K.

$$\theta_w^{\mathrm{dip}} = -\frac{\mu_B^2}{4Pk_Ba^3}[-g_\perp^4(141.00) + g_\perp^2 g_\parallel^2(140.50) + g_\parallel^4(0.50)]. \quad (1)$$

In this formula a is the cubic unit cell edge, $g_\parallel$ and $g_\perp$ are the diagonal elements of the axially symmetric g tensor of the ground doublet of the rare-earth ion, and $P = (g_\parallel^2 + 2g_\perp^2)/3$. The small size of the final term in this expression is due to the peculiar structure of the KY_3F_{10} materials, and indicates that θ_w^{dip} by itself is not a good indicator of the strength of dipolar interactions when the moment is Ising-like. The g factors have been measured by paramagnetic resonance to be $g_\parallel = 10.85$, $g_\perp < 1.5$.[11] This leads to $0.017\ \mathrm{K} < \theta_w^{\mathrm{dip}} < 0.105$ K, so $\theta_w = \theta_w^{\mathrm{ex}}$ within experimental accuracy and exchange is antiferromagnetic in this material.

Because the observed ordering feature in the susceptibility appeared to be in conflict with the inferred antiferromagnetic exchange in KDy_3F_{10}, the magnetization was measured as a function of external magnetic field at a temperature of ~30 mK, well below the ordering feature in the susceptibility. A very sharp-cornered hysteresis loop was observed. The data are shown in Fig 3. A small remanent magnetization of about $0.18\mu_B$/ion is present, indicating that KDy_3F_{10} indeed has a polarized ground state, though it cannot be a simple ferromagnetic one. At the higher temperature of 135 mK, hysteresis was no longer observable. At this temperature we estimate the saturation moment to be an order of magnitude higher, at least $1.8\mu_B$/ion, with the saturation field exceeding 0.2 T.

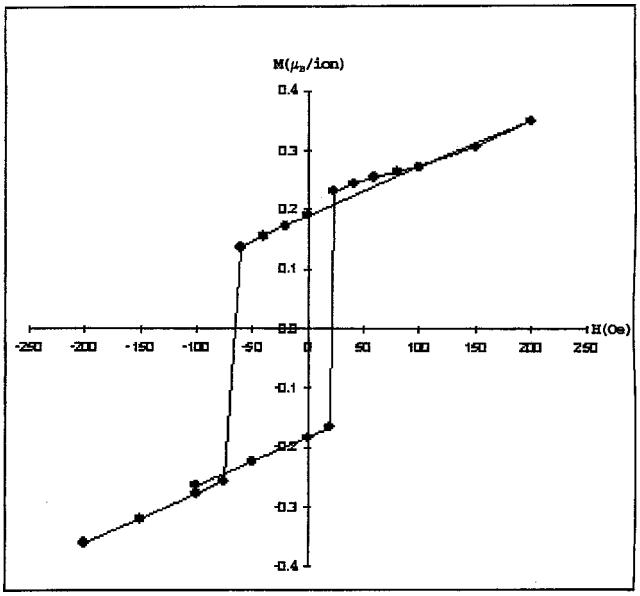

FIG. 3. Magnetization as a function of H for KDy_3F_{10} at $T \cong 30$ mK. A sharp-cornered hysteresis loop is visible, with a small remanent moment.

Some insight into these results can be obtained from a numerical energy minimization calculation of the magnetic Hamiltonian at $T=0$. If we make the simplifying assumption of isotropic exchange in KDy_3F_{10}, the Hamiltonian is[12,13]

$$H=\frac{1}{2}\sum_{ij}\frac{1}{r_{ij}^3}\left[\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j-3\frac{(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right]$$

$$-\sum_{ij}J_{ex}\mathbf{S}_i\cdot\mathbf{S}_j-D\sum_i S_{i\|}^2, \qquad (2)$$

where $\boldsymbol{\mu}_i=\mu_B[\mathbf{g}_i]\mathbf{S}_i$, $[\mathbf{g}_i]$ is the local g tensor for spin i[14,15] and nearest neighbor exchange is assumed, but the dipolar interaction is long ranged. D is a single-ion anisotropy coefficient and $S_{i\|}$ denotes the component of $\mathbf{S}_i$ parallel to the local tetragonal symmetry axis. The crystal field is responsible both for D and for the anisotropy in the g tensor. From spectroscopically determined crystal field parameters,[11] the first excited state of Dy^{3+} in KDy_3F_{10} occurs 13 K above the ground doublet. Above this temperature, the calculated single-ion susceptibility is much less anisotropic, implying an effective anisotropy constant D of order 10 K. The exchange constant is obtained from $\theta_w^{\rm ex}=2zS(S+1)J_{\rm ex}/3k_B$,[16,17] where the number of nearest neighbors z for this structure we take to be 8, and the effective spin S of the ground doublet of Dy^{3+} is $\frac{1}{2}$. Strictly speaking, $z=4$ because neighboring octahedra differ slightly in size, but the difference is less than 8%. This yields $J_{\rm ex}=-0.325\pm0.5$ K. The last term in the Hamiltonian, the single ion anisotropy term, is therefore large compared to the interaction terms, and the spins (assumed Heisenberg-like in the beginning) will be nearly aligned with their local symmetry axes. Due to the large magnetic moment of the Dy^{3+} ion, the assumption of semiclassical spins is reasonable. If we assume the alignment is complete, so that the spins are perfectly Ising-like, the exchange term will be identically zero, since nearest-neighbor spins are all orthogonal.

It is instructive to first minimize the Hamiltonian assuming $J_{\rm ex}=0$. A random set of orientations for the spins in the cubic unit cell (24 for the KY_3F_{10} structure) is selected. For each spin arrangement, dipolar energy calculations were made using the Ewald-Kornfeld method. The energy was then minimized using the conjugate gradient method,[18] varying all 24 spin orientations until an energy minimum is found. This process is repeated several hundred times until all minima are located, the lowest one taken to be the ground state. For the case of isotropic moments (equivalent spins), this result could be checked against the prediction of the Luttinger-Tisza method[19] and was found to agree accurately. This procedure predicts a dipolar ground state which is antiferromagnetic, with a dipolar energy per spin of -0.552 K. (There is no general correlation between the sign of $\theta_w^{\rm dip}$ and the type of dipolar ground state, in the absence of exchange.)[9] This dipolar energy is comparable to $J_{\rm ex}$, indicating that the intrinsic magnitudes of the two interactions are similar in size. This ground state consists of a collinear arrangement of spins along each of the three cubic axes, alternating individually up and down along two of the axes (e.g., x and y) but forming alternating head-to-tail chains along the third (z), and disagrees with experiment. Unlike the $LiYF_4$ materials, the ordered state in KDy_3F_{10} cannot be predicted by the dipolar interaction alone.

In the absence of exchange, a ferromagnetic energy minimum lies approximately 20 mK higher than the antiferromagnetic ground state described above, and differs only in that the head-to-tail chains along the z axis do not alternate but are all polarized up or down, producing a net moment of $8g_{\|}\mu_B S$ per unit cube along one of the cubic axes. This spin arrangement is pictured in Fig. 4. We now gradually turn on the exchange term and observe how these two dipolar states are modified. So long as the spins are completely aligned along their anisotropy axes, nearest neighbor exchange remains zero, and second neighbor exchange, between spins on opposite vertices of a rare earth octahedron, merely raises or lowers both states by the same amount. If the x and y axis spins rotate slightly away from their Ising axes, so that spin $\mathbf{S}$ has a small orthogonal component $\mathbf{S}_\perp$, we can now understand qualitatively how a ferromagnetic state is stabilized by the presence of antiferromagnetic exchange. To first order in $S_\perp$ the anisotropy energy is unchanged, as is the dipolar energy because $g_\perp \approx 0$. However, the exchange energy for a single canted spin is changed by $-J_{\rm ex}\mathbf{S}_\perp\cdot\Sigma_{nn}\mathbf{S}_j$. This term is zero for the antiferromagnetic ground state because the summation over nearest neighbor spins is zero to lowest order. For the ferromagnetic spin arrangement the sum is nonzero, on average. Therefore by canting slightly away from the polarized head-to-tail chains of spins, the alternating spins along the other two cubic axes can reduce the exchange energy of the system while hardly affecting the dipolar and anisotropy energies. The decrease in average energy, per spin, is given for $(S_\perp/S)\ll 1$ by

$$\Delta\varepsilon\cong J_{\rm ex}n_1SS_\perp+S_\perp^2(\tfrac{2}{3}D-Q_d-J_{\rm ex}n_2), \qquad (3)$$

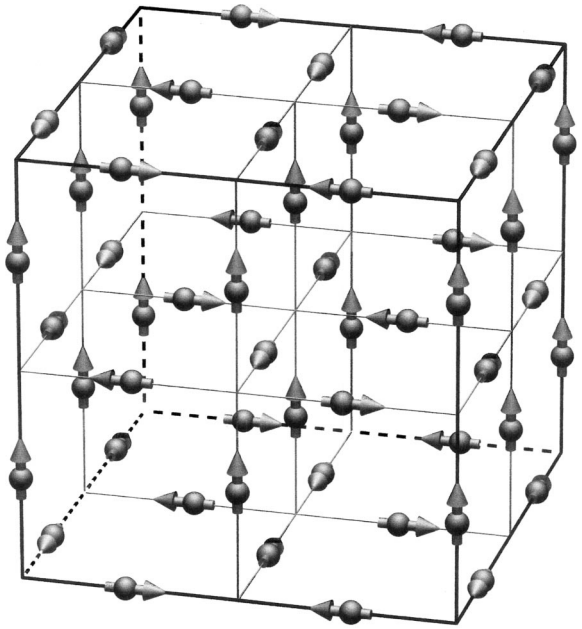

FIG. 4. Dipolar ferromagnetic state lying approximately 20 mK above the antiferromagnetic ground state, obtained by minimizing the Hamiltonian of Eq. (2) with $J_{ex}=0$. Only the magnetic Dy^{3+} spins within the cubic unit cell are shown. The ground state differs from that pictured in that the vertical chains of spins alternate up and down.

where n_1 is the average number of $S_\perp$-$S_\parallel$ bonds per spin, n_2 is the average number of $S_\perp$-$S_\perp$ bonds per spin, and Q_d is a dipolar energy sum equal to -1.796 K for KDy_3F_{10}. For this state $n_1=\frac{16}{3}$ and $n_2=\frac{8}{3}$. If the magnitude of J_{ex} is sufficiently large, the energy of the ferromagnetic state will drop below the antiferromagnetic one. By minimizing the energy per spin with respect to $S_\perp$, we estimate that this occurs for $J_{ex}\cong-2([\frac{2}{3}D-Q_d]\Delta)^{1/2}/n_1S$, where Δ is the splitting between the ferromagnetic and antiferromagnetic dipolar states in the absence of exchange. For KDy_3F_{10} this predicts a ferromagnetic state for $J_{ex}<\sim(-0.3\ \mathrm{K})$, which is satisfied by the experimental value. Using the experimental $J_{ex}=-0.325$ K, we obtain $S_\perp/S\cong-J_{ex}n_1/2(\frac{2}{3}D-Q_d)\approx0.1$ and $\Delta\varepsilon\cong-0.022$ K, so the predicted deviation from Ising-like symmetry is small, and the overall spin-spin interaction energy is predominantly dipolar in origin. This is a consequence of the peculiar structure of KDy_3F_{10}, which strongly reduces the magnitude of the exchange energy due to single-ion anisotropy. This predicted state differs from conventional weak ferromagnetism,[20] which typically involves only exchange, and which results from a slight canting of two antiferromagnetic sublattices by an anisotropic perturbation which is small compared to the exchange energy. In KDy_3F_{10}, exchange is constrained by the large single-ion anisotropy to be small compared to the dipolar energy.

The average saturation moment per ion along a cubic axis for this arrangement is $M_{ion}\cong g_\parallel\mu_B S/3=1.81\mu_B$. Subsidiary local energy minima are found at higher energies which correspond to states with smaller polarizations. These have, on average, one through seven spins per cubic unit cell aligned along a single cubic axis. The value of the experimental remanent moment, $0.18\mu_B$/ion, is most consistent with a state containing the minimum polarization of one spin per cell, corresponding to two head-to-tail chains out of every sixteen polarized along the z axis. Because the energy splitting between the polarized states is only of order 10 mK, an applied field of order 10 mT can cause a transition from one to the other. For this reason, the magnitude of the saturation moment at $H\gg10$ mT does not allow us to determine which state we observe at low field. The discrepancy between calculation and experiment is possibly due to the existence of anisotropic exchange in KDy_3F_{10}. While simplified, this procedure is nevertheless useful in understanding how the sum of two interactions, each of which favors an antiferromagnetic ground state in the absence of the other, can lead to a ground state which is polarized.

In conclusion, we have measured the magnetic properties of KDy_3F_{10}, a cubic system with axial moments nearly aligned along three mutually orthogonal Ising lattices. Susceptibility measurements indicate that exchange is antiferromagnetic, and calculation shows that the dipole-dipole interaction alone also favors an antiferromagnetically ordered state. Despite this, the material orders in a state with a spontaneous magnetization. By numerically minimizing the Hamiltonian at $T=0$, we find that this result is to be expected when the ratio of exchange to dipolar interaction strength lies in a certain range.

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*Present address: Boxer Cross, Inc., Menlo Park, CA 94025.

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