Anisotropic paramagnetic response of hexagonal $RMnO_3$

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The anisotropic paramagnetic susceptibility of single crystals of the hexagonal manganites $RMnO_3$ (R=Ho, Er, Tm, Yb, and Lu) is studied. It is found that the anisotropy of the paramagnetic Curie temperature along the sixfold axis and in the basal plane, $\theta_{\parallel}-\theta_{\perp}$, is determined not by the anisotropic Mn-O-Mn interactions but rather by the quadrupolar charge distribution of the 4f shells of the rare-earth ions. These findings disclose the decisive role of the R ions in forming the paramagnetic behavior of $RMnO_3$ and suggest a subtle interplay between the *charge-density* distribution of rare-earths and the symmetry of the *spin-ordering* of the Mn sublattices.

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Following the boom of research into high-temperature superconductivity, the interest in rare-earth oxides has been further fueled by the revival of giant magnetoresistance and more recently of magnetoelectric phenomena. Almost half a century ago Bertaut *et al.* reported that long-range magnetic and polar orders could coexist in the hexagonal family of the $RMnO_3$ oxides.[1] The Mn^{3+} ions occupy the 6c positions in the hexagonal structure of $RMnO_3$ (space group $P6_3cm$); the surrounding of each Mn^{3+} has trigonal symmetry and consists of three in-plane and two apical O^{2-} ions. The magnetic order of the Mn moments is determined by antiferromagnetic in-plane Mn-O-Mn superexchange, which is much stronger than the interplane Mn-O-O-Mn exchange. As a result, at T_N, the Mn moments order in a 120° arrangement within the basal plane, typical for frustrated triangular antiferromagnets. The Mn subsystem has been so far the center of attention, while the presence of rare-earth ions was largely overlooked, except in a few studies conducted at very low temperatures. The R ions occupy two different sites: 2a and 4b. Their magnetic moments eventually order at much lower temperatures than those of Mn. The magnetic structure and the interactions of the R sublattice remain largely unexplored, except for $HoMnO_3$ and $ErMnO_3$, where neutron-diffraction[2–5] and second-harmonic generation[6] experiments suggest that at zero magnetic field the R moments order along the hexagonal axis, and the bulk magnetization study[7] suggests that they are arranged in triangular structure within the c plane.

As far as the paramagnetic susceptibility of the hexagonal $RMnO_3$ is concerned, the presence of rare-earth ions was mainly ignored despite the fact that the R contribution to the key quantity—the Curie constant C—could be as high as 80% of the total. At most it was noticed that the extrapolated paramagnetic Curie temperature θ increases with the atomic number of R (Ref. 8) and that doping $YMnO_3$ with a magnetic rare earth raises the effective magnetic moment μ_{eff} and depresses θ,[9] without relating these quantities to any particular atomic species. No attention was paid to the shape—as opposed to size—of the 4f shell of the rare earths. This shape is specific to each rare-earth element and in the simplest approximation is described by a single quantity—the Stevens factor α_J.[10] This factor is known to play a decisive role in the magnetocrystalline anisotropy of rare-earth metals and intermetallics. In oxides, which are predominantly antiferromagnetic, another contributor to the anisotropy may be important—the non-Heisenberg 3d-4f exchange. In this connection it is instructive to recall rare-earth orthoferrites $RFeO_3$, where anisotropic R-Fe exchange is instrumental in bringing about a wealth of spin-reorientation transitions including those above room temperature.[11]

Magnetic properties of these highly anisotropic compounds have to be studied on single crystals. Several such studies have been carried out; they all found the paramagnetic Curie temperature deduced from the susceptibility along the sixfold axis ($\theta_{\parallel}$) to have a larger negative value than that deduced from the basal-plane data ($\theta_{\perp}$): $|\theta_{\parallel}|>|\theta_{\perp}|$. This relation was reported in particular for R=Ho,[12] Er,[13] and Yb.[14] One is inclined to see here a manifestation of geometric in-plane frustration within the Mn subsystem[12] measured by the ratio $|\theta|/T_N$.[15] However, this simple explanation runs into difficulties as soon as one recalls that θ is largely a property of the rare-earth subsystem rather than of the Mn one.

In this Brief Report we address the anisotropic magnetic properties of $RMnO_3$ single crystals in the paramagnetic range, unveiling the long standing problem of the anisotropy of extrapolated Curie temperatures in hexagonal $RMnO_3$ oxides. We show that the difference $\theta_{\parallel}-\theta_{\perp}$ depends in a characteristic way on the atomic number of the rare earth with a

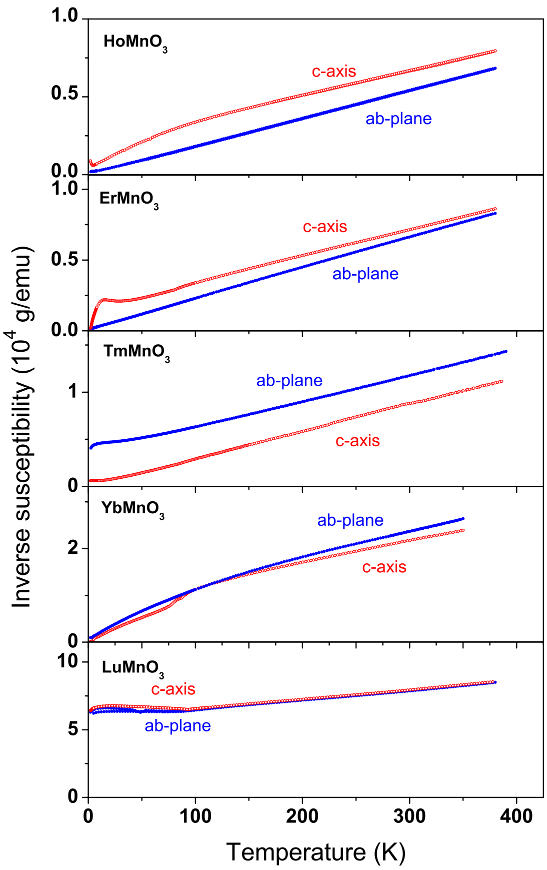

FIG. 1. (Color online) Temperature dependence of the inverse principal susceptibilities of hexagonal RMnO$_3$ single crystals.

change of sign between Ho and Er. These findings disclose the dramatic relevance of the rare earths with particular emphasis on the role of the anisotropic charge distribution of their 4f shells in the magnetic properties of these compounds.

RMnO$_3$ (R=Ho, Er, Tm, Yb, and Lu) plateletlike single crystals were grown by the flux method from high-temperature solution as described elsewhere.[13] Structural characterization was performed by means of Laue x ray as well as by neutron diffraction. In all cases the space group was found to be the hexagonal $P6_3cm$, with refined lattice parameters being in agreement with the published data. No structural change was observed between T=4.2 K and T=300 K. Naturally shaped as-grown crystals in the form of a hexagon (with a mass of about 0.01 g and 0.5 mm thick) have been chosen for magnetic study. dc magnetic susceptibility was measured by a superconducting quantum interference device magnetometer (Quantum Design MPMS XL) at temperatures between 2 and 380 K in an applied field of 1 kOe. The data reported here were corrected for the demagnetizing field effect (demagnetizing factors $N_\parallel \approx 0.9$ and $N_\perp \approx 0.1$).[16]

Figure 1 displays the temperature dependence of the inverse principal susceptibilities of the hexagonal RMnO$_3$. The susceptibility of LuMnO$_3$ (Lu^{3+} is diamagnetic) appears almost isotropic, in sharp contrast to the anisotropic susceptibility of the RMnO$_3$ with "magnetic" rare earths. HoMnO$_3$ and TmMnO$_3$ are paradigms of a positive and a negative ($\chi_\parallel^{-1}-\chi_\perp^{-1}$), respectively. The results shown in Fig. 1 already evidence that the sign of ($\chi_\parallel^{-1}-\chi_\perp^{-1}$) cannot be a simple measure of the magnetic susceptibility of the Mn sublattice but it is dominated by the rare-earth response. On the other hand, overall, the curves presented in Fig. 1 are only approximately linear. One may note that in each one of the top four panels the lower curve shows a better linearity across a wider temperature range than the upper one. For every RMnO$_3$ studied the Curie constant C, determined from the high-temperature slope of the lower curve (C=64, 47, 35, 21, and 12 mK emu/g for R=Ho, Er, Tm, Yb, and Lu, respectively), proved very close to a sum of the free-ion values for Mn^{3+} (S=2, spin only) and R^{3+}. This was not always the case for C's deduced from the upper curves.

It is important to realize that the true Curie-Weiss behavior, characterized by the free-ion C, sets in well above room temperature, when all the levels of the crystal-field-split ground multiplet of R^{3+} are significantly populated. In the high-temperature regime, $\chi_{\parallel,\perp}^{-1}(T)$ is supposed to be a pair of parallel straight lines sloping at $1/C$. Of particular interest to us here is the displacement between these lines along the temperature axis, $\theta_\parallel-\theta_\perp$. This quantity is a fingerprint that will eventually enable us to identify the rare-earth ions as the key factor in the room-temperature magnetism of RMnO$_3$. Making the fingerprint ultimately sharp involves extrapolation of the room-temperature data to infinitely high temperature. To this end we use the high-temperature expansion of the difference of the inverse principal susceptibilities,[17]

$$(\chi_\parallel^{-1}-\chi_\perp^{-1}) = -(\theta_\parallel-\theta_\perp)C^{-1} + (A_\parallel - A_\perp)T^{-1} + (B_\parallel - B_\perp)T^{-2} + \cdots. \quad (1)$$

Here $A_{\parallel,\perp}$ and $B_{\parallel,\perp}$ are coefficients in the high-temperature expansions of $\chi_\parallel^{-1}$ and $\chi_\perp^{-1}$. The difference $\theta_\parallel-\theta_\perp$ was determined by plotting ($\chi_\parallel^{-1}-\chi_\perp^{-1}$) against $1/T$ and extrapolating to $1/T=0$, as shown in Fig. 2 for some representative samples (R=Ho, Er, and Yb). The extrapolation appears essential for the correct determination of $\theta_\parallel-\theta_\perp$, especially in the case of ErMnO$_3$, where the two principal susceptibilities cross over at about 600 K (Fig. 2). An added advantage of the ($\chi_\parallel^{-1}-\chi_\perp^{-1}$) vs $1/T$ graphs is that they help visualize such a subtle feature as T_N, which is hardly discernible in the χ^{-1} vs T plots (Fig. 1).

The so determined $\theta_\parallel-\theta_\perp$ values are shown as open circles in Fig. 3. An open square and a diamond in the same figure indicate, respectively, $\theta_\parallel-\theta_\perp$ deduced in a similar fashion from the data of Refs. 18 and 19 and pertaining to a structurally metastable hexagonal DyMnO$_3$. One observes that $\theta_\parallel-\theta_\perp$ depends in a regular fashion on R and changes sign between Ho and Er. The meaning of the quantity $\theta_\parallel-\theta_\perp$ can be appreciated in the framework of the crystal-field theory, where it is directly related to the leading rare-earth crystal-field parameter A_{20} through a classical formula due to Elliott[20]

$$\theta_\parallel-\theta_\perp = -\tfrac{3}{10}(2J-1)(2J+3)\alpha_J A_{20}\langle r^2\rangle. \quad (2)$$

Here $\langle r^2\rangle$ is the 4f radial expectation value and α_J stands for the second-order Stevens factor. The product $A_{20}\langle r^2\rangle$ is usually regarded as a single parameter. In the hexagonal RMnO$_3$

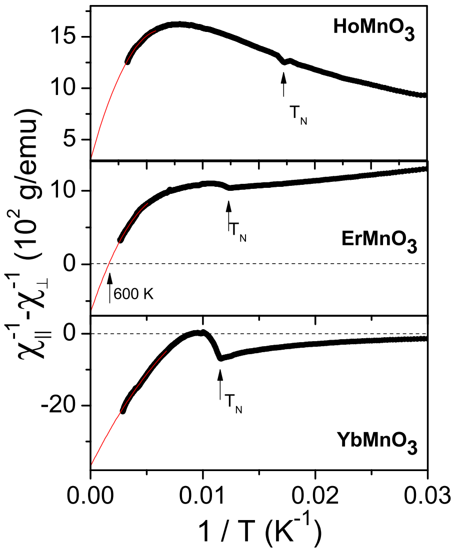

FIG. 2. (Color online) Temperature dependences of the difference in the inverse susceptibilities versus inverse temperature for some representative $R\mathrm{MnO_3}$. The thin line is a parabolic fit of the high-temperature data extended to $1/T=0$.

the rare-earth ions occupy two nonequivalent sites, $2a$ and $4b$. Therefore, in relation to these compounds A_{20} should be understood as a weighed average $A_{20}=\frac{1}{3}A_{20}(2a)+\frac{2}{3}A_{20}(4b)$.

Let us transform the Elliott formula (2) limiting ourselves to the ground multiplet of a trivalent heavy rare-earth ion. We consider the ground configuration $4f^N$, where N is the number $4f$ electrons, $7<N<14$. This number, regarded as a continuous variable, is better suited for studying the trends across the rare-earth series than the discrete quantum numbers S, L, and J. The latter can be expressed in terms of N by means of the three Hund's rules:

$$S=\tfrac{1}{2}(14-N),$$

$$L=S(N-7)=\tfrac{1}{2}(N-7)(14-N),$$

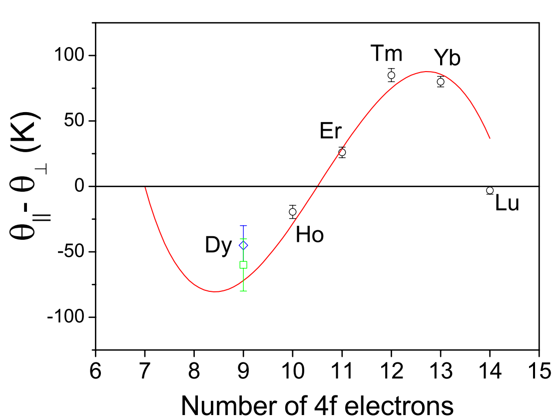

FIG. 3. (Color online) The difference of the principal paramagnetic Curie temperatures versus the number of $4f$ electrons in the ground configuration of R^{3+}. Open circles: this work; open diamond: deduced from the data of Ref. 17; open square: deduced from the data of Ref. 18. The solid curve is Eq. (7) times -2 K.

$$J=L+S=\tfrac{1}{2}(N-6)(14-N). \tag{3}$$

For the Stevens factor of a heavy rare-earth ion the following expression holds:[21]

$$\alpha_J=\alpha_L\frac{L(2L-1)}{J(2J-1)}=\frac{2}{45}\frac{L(7-4S)}{J(2J-1)}, \tag{4}$$

where α_L is a numerical factor given by[22]

$$\alpha_L=\frac{2}{45}\frac{7-4S}{2L-1}. \tag{5}$$

Since its denominator vanishes at $N=14$, Eq. (4) does not apply to $\mathrm{Lu^{3+}}$ nor do Eqs. (6) and (7) below.

Eliminating the quantum numbers from Eq. (4) by means of the Hund's rules (3) and substituting the resulting Stevens factor into Elliott's formula (2), we finally get

$$\theta_\parallel-\theta_\perp=\tfrac{1}{75}f_N A_{20}\langle r^2\rangle, \tag{6}$$

where

$$f_N=(N-7)(2N-21)\left(N-14-\frac{3}{N-6}\right). \tag{7}$$

According to this result, the quantity $\theta_\parallel-\theta_\perp$ should follow the same dependence on N as the numerical factor f_N. A good agreement, including a change of sign between $N=10$ and 11, can indeed be observed in Fig. 3, where the solid curve is just Eq. (7) times -2 K. This confirms the statement made above that the anisotropic magnetic properties of $R\mathrm{MnO_3}$ in the room-temperature range are governed predominantly by the second-order crystal field on the rare-earth sites. The average crystal-field parameter is estimated as $A_{20}\langle r^2\rangle=-150$ K. This is in a fair agreement with the average over the two sites in $\mathrm{YbMnO_3}$, $A_{20}\langle r^2\rangle=-180$ K, deduced from the infrared absorption spectra.[23] The single crystals investigated in this Brief Report and in Ref. 23 came from the same batch. Note that the values quoted in the table caption of Ref. 23 have to be divided by two (apart from the conversion of units and averaging over the two sites) in order to be transformed to the Stevens convention adopted herein.

Recapitulating our main findings, the paramagnetic susceptibility of the hexagonal manganites $R\mathrm{MnO_3}$ is strongly anisotropic for those R which have an open $4f$ shell in a trivalent state: R=Dy, Ho, Er, Tm, and Yb. The sign of the difference $\theta_\parallel-\theta_\perp$ is determined by the sign of the Stevens factor α_J, which is a measure of the quadrupolar charge distribution (prolate or oblate shape) within the R ions. As against that, $\mathrm{LuMnO_3}$ is practically isotropic above T_N. The strong anisotropy in the former case means difference of the paramagnetic Curie temperatures for the two principal crystallographic directions, whereas the Curie constant C is practically isotropic and equal to a sum of free-ion contributions from R^{3+} and $\mathrm{Mn^{3+}}$ (in $\mathrm{ErMnO_3}$ and $\mathrm{YbMnO_3}$ C becomes truly isotropic only well above room temperature). The paramagnetic Curie temperatures, $\theta_\parallel$ and $\theta_\perp$, are largely characteristics of the rare-earth subsystem, because the rare-earth contribution to C is prevalent when nonzero. At any rate, the purely spin magnetism of the $\mathrm{Mn^{3+}}$ ions appears to have no bearing on the difference $\theta_\parallel-\theta_\perp$. It should be emphasized again that the Curie-Weiss law under examination pertains to the high-temperature regime. Any short-range order effects in the Mn subsystem[5,8] would have died out at such temperatures. The anisotropic Mn-R exchange, important as it may be below T_N, is too weak to seriously affect the paramagnetic susceptibility in the room-temperature range. It is clear from the above discussion that the ratio of θ (essentially a property of R) to T_N (a property of Mn) cannot be regarded as a measure of frustration—the inference[9] from magnets with a single kind of magnetic atoms does not apply to $RMnO_3$.

The variation in $\theta_\parallel - \theta_\perp$ across the rare-earth series is described by Eq. (6). Accordingly, $\theta_\parallel - \theta_\perp$ changes sign between Ho and Er. The underlying reason is that the charge distribution in Ho^{3+} has an oblate shape, whereas it is prolate in the heavier magnetic rare-earth ions, Er^{3+}, Tm^{3+}, and Yb^{3+}. This fact, overlooked so far, may provide a clue as to why the Mn^{3+} ions (also endowed with an anisotropic charge distribution) prefer one magnetic configuration ($P6_3'cm'$) in the presence of oblate or spherically symmetric rare-earth ions (Ho^{3+} or Lu^{3+}) but a different magnetic configuration ($P6_3'c'm$) in the compounds with the prolate Er^{3+}, Tm^{3+}, or Yb^{3+}.[24,25] We believe it to be a clear manifestation of a strong Mn-R quadrupole-quadrupole interaction in $RMnO_3$.

In summary, we have shown that in biferroic hexagonal $RMnO_3$ oxides the paramagnetic susceptibility, the extrapolated Curie temperatures, and their anisotropy $\theta_\parallel - \theta_\perp$ are determined by the quadrupolar charge distribution of the 4f rare-earth atomic shells, itself determined by the crystal field. This fundamental contribution, which had been neglected so far, while solving long-time open questions about magnetic properties of hexagonal oxides, also illustrates the subtle interplay between the *charge-density* distribution of rare earths and the symmetry of the *spin ordering* within the Mn and the rare-earth sublattices.

Note added in proof: We have become aware of some unpublished results from the Ph.D. thesis of Dana Tomuta (Leiden University, 2003) which are in agreement with our study. We are grateful to Sahana Rößler for bringing to our attention part of this thesis.

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