

Ising-Like Spin Anisotropy and Competing Antiferromagnetic-Ferromagnetic Orders in $\text{GdBaCo}_2\text{O}_{5.5}$ Single Crystals

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In $\text{RBaCo}_2\text{O}_{5+x}$ compounds (R is rare earth), a ferromagnetic-antiferromagnetic competition is accompanied by a giant magnetoresistance. We study the magnetization of detwinned $\text{GdBaCo}_2\text{O}_{5.5}$ single crystals and find a remarkable uniaxial anisotropy of Co^{3+} spins which is tightly linked with the chain oxygen ordering in $\text{GdO}_{0.5}$ planes. Reflecting the underlying oxygen order, CoO_2 planes also develop a spin-state order consisting of Co^{3+} ions in alternating rows of $S = 1$ and $S = 0$ states. The magnetic structure appears to be composed of weakly coupled ferromagnetic ladders with Ising-like moments, which gives a simple picture for magnetotransport phenomena.

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Transition-metal oxides exhibit a complex interplay between charge, spin, orbital, and lattice degrees of freedom, which is at the heart of many fascinating phenomena such as colossal magnetoresistance (MR) in manganites. Phenomenologically, the colossal MR originates from a magnetic-field induced transition between delicately balanced and competing phases that dramatically differ in resistivity [1]. However, the microscopic origin of these competing phases still remains far from being clear, owing to the complexity of the manganites; for example, magnetic fields [which induce a ferromagnetic (FM) spin alignment in manganites] have been found to melt the charge order [2], change the orbital order with accompanying Jahn-Teller distortions [3], and modify the scale and topology of domains in microscopically heterogeneous phases [1,4].

In order to clarify the MR mechanisms operating in transition-metal oxides, one may look for compounds that also exhibit competing phases and giant MR, but possess fewer degrees of freedom. Recently, an intriguing anti-ferromagnetic (AF)—ferromagnetic competition accompanied with a giant MR has been found in cobalt-oxide compounds $\text{RBaCo}_2\text{O}_{5+x}$ (where R is rare earth) [5–8]. While cobaltites with a variable spin state of Co ions [5–11] are in general no simpler than manganites, $\text{RBaCo}_2\text{O}_{5+x}$ with $x \approx 0.5$ possesses plenty of attractive features that may turn it into a model system. For $x \approx 0.5$, oxygen ions in RO_x layers order into alternating filled and empty rows running along the a axis [5,8,9], thus allowing one to deal with an almost perfect crystal structure. No considerable structural distortions are detected at the AF-FM transition as well [9,12]. Moreover, at $x \approx 0.5$ the valence state of Co ions approaches $3+$, so that charge ordering and electronic phase separation typical for mixed-valence systems [1] become irrelevant for this composition.

In this Letter, we present a first study of the static magnetization in detwinned $\text{GdBaCo}_2\text{O}_{5.5}$ single crystals. We find a strong Ising-like spin anisotropy which is

clearly manifested in the FM phase, where Co spins are aligned along the oxygen-chain direction with a net magnetic moment of $\sim 1 \mu_B/\text{Co}$. This value indicates a 1:1 ratio of Co^{3+} ions in the $S = 0$ and $S = 1$ spin states; based on this result and a recent structural study [13], we propose that the oxygen-chain ordering causes the $S = 1$ Co^{3+} ions to be arranged into ferromagnetic 2-leg ladders that are separated by nonmagnetic layers. The AF-FM competition and giant MR in $\text{GdBaCo}_2\text{O}_{5.5}$ appear to reflect a relative magnetic order among weakly coupled FM ladders, which can be rather easily altered by temperature or magnetic fields.

Using the floating-zone technique, we have succeeded in growing high-quality $\text{GdBaCo}_2\text{O}_{5+x}$ single crystals suitable for magnetization and transport measurements. The crystals were annealed in a flow of oxygen at 470°C , the temperature being carefully tuned [14] to provide the oxygen stoichiometry $x = 0.50$. Parallelepiped samples with all faces adjusted to the crystallographic planes with a 1° accuracy were prepared by cutting and polishing under Laue x-ray diffraction control. In $\text{GdBaCo}_2\text{O}_{5.5}$, the oxygen ordering in $\text{GdO}_{0.5}$ planes induces a tetragonal-to-orthorhombic transition, which is accompanied by heavy twinning of crystals that mixes the a and b orthorhombic axes. To detwin crystals, we slowly cooled them under a uniaxial pressure of ~ 0.15 GPa from 260°C , using an optical microscope to control the twin removing [15]; note that these crystals are fragile and only few survive the detwinning procedure. According to x-ray measurements, the remaining fraction of misoriented domains (which characterizes the quality of detwinning) was 4%–5%. Magnetization measurements were carried out using a SQUID magnetometer at fields up to 7 T applied along the a , the b , or the c axis. Throughout this paper, the magnetization coming from Co ions is determined by subtracting the contribution of Gd ions, assuming their ideal paramagnetic (PM) behavior with total spin $S = 7/2$ [see inset in Fig. 1(a)]; the latter is a good approximation since no ordering of

Gd^{3+} moments is detected down to 1.7 K. The magneto-resistance was measured by a four-probe method on twinned crystals.

Figure 1(a) shows the magnetization of untwinned $\text{GdBaCo}_2\text{O}_{5.5}$ single crystals measured along a , b , and c axes in the field-cooling process. Below 300 K, a net ferromagnetic component appears in the Co sublattice and suddenly vanishes at ~ 260 K, indicating successive PM-FM-AF transitions [5–9]. A remarkable feature of the FM state is not only the narrow temperature window where it shows up, but also a very strong anisotropy: We have found that the net FM moment appears only along the a axis, and even the 7-T field is not enough to turn over the magnetic moment along the b or c axis. Note that a small magnetization along the b axis in Fig. 1(a) comes mostly from residual misoriented domains. This behavior suggests the spin system in $\text{GdBaCo}_2\text{O}_{5.5}$ to be *Ising like*, which drastically simplifies the understanding of magnetic ordering.

The balance of FM and AF ordering in $\text{GdBaCo}_2\text{O}_{5+x}$ turns out to be quite delicate and can be easily affected by temperature, magnetic fields, or even subtle variation in stoichiometry. Magnetic fields applied along the spin-easy a axis stabilize the FM state and shift the FM-AF transition to lower temperatures [Fig. 1(b)]. Nevertheless, it would not be correct to consider the FM and AF orders as simply competing ones. If this switching were originating from equally strong and competing AF and FM exchange interactions, spin fluctuations would inevitably be enhanced in the vicinity of the FM-AF phase boundary, smearing the transition. Isothermal magnetization curves in Fig. 2(a) demonstrate, however, that although the FM-AF balance is subtle, and fairly weak

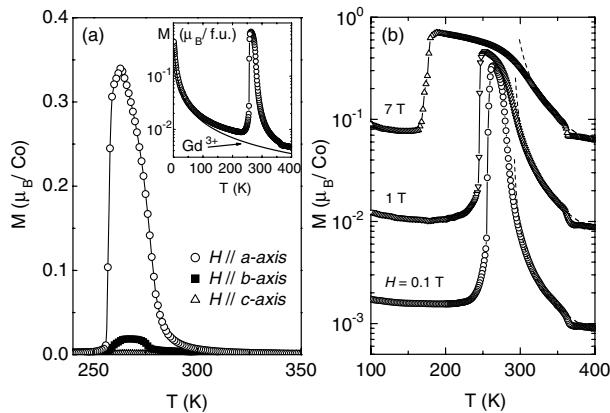


FIG. 1. (a) Magnetization of an untwinned $\text{GdBaCo}_2\text{O}_{5.5}$ crystal measured in $H = 0.1$ T applied along one of the crystal axes (contribution of Gd^{3+} ions is subtracted). Inset: raw $M(T)$ data for $H \parallel a$, where the solid line shows the Curie-Weiss contribution of Gd^{3+} ions ($\mu_{\text{eff}} = 7.94 \mu_B$; $\theta = 0$ K). (b) $M(T)$ in different magnetic fields $H \parallel a$. Kinks at $T \approx 360$ K correspond to the metal-insulator transition. Dashed lines are Curie-Weiss curves with $\mu_{\text{eff}} = 2 \mu_B/\text{Co}$ and $\theta = 290$ K.

fields (~ 1.5 T at 240 K) are capable of recovering the FM order, the AF-FM transition remains always sharp, showing that thermal fluctuations are irrelevant here. This behavior clearly indicates that the observed AF-FM switch occurs *within* the ordered spin state and is governed by the reorientation of spins in one of the weakly coupled sublattices.

The fact that the AF-FM transition remains sharp, even when it is induced by a weak field $\mu_B H \ll kT$ [Fig. 2(a)], unambiguously points to a strong hierarchy of spin interactions in $\text{GdBaCo}_2\text{O}_{5.5}$. A strong ferromagnetic interaction aligns spins within each sublattice, while a much weaker antiferromagnetic (at $T < 260$ K) interaction provides a subtle coupling between the sublattices, which can be broken by an applied field. Figure 2(c) shows that a magnetic field $H \parallel a$ required to overcome the AF coupling grows roughly linearly upon cooling, from zero at $T \approx 260$ K up to ~ 20 T at $T = 0$ [Fig. 2(c)]. Whatever the temperature, however, the 7-T field, $H \parallel b$ or $H \parallel c$, cannot compete with the spin anisotropy and causes just a partial tilting of spins (in each sublattice) from their easy axis, thus giving linear $M(H)$ curves in both FM and AF regions [Fig. 2(b)].

Qualitatively, the overall magnetic behavior is quite reminiscent of that in canted antiferromagnets, such as La_2CuO_4 [16], where slight spin canting brings about a weak ferromagnetism. However, the magnitude of the field-induced FM moment, reaching $\sim 0.6 \mu_B/\text{Co}$ at $T = 205$ K [Fig. 2(a)], is apparently inconsistent with such weak spin canting and points to a different origin of the

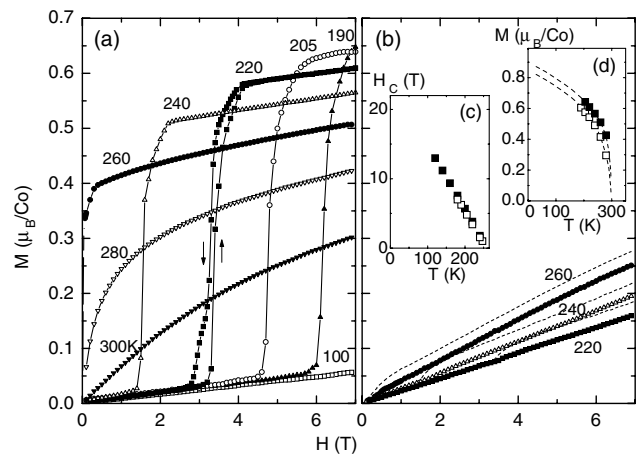


FIG. 2. Isothermal magnetization of $\text{GdBaCo}_2\text{O}_{5.5}$ for (a) $H \parallel a$, (b) $H \parallel b$. In (b), dashed lines indicate the experimental data, and symbols show $M(H)$ after subtracting the contribution from misoriented domains (4% of the total amount). Inset (c): critical magnetic fields H_c for the AF-FM transition obtained from magnetization (open squares) and magnetoresistance (solid squares). Inset (d): net magnetic moment along the a axis measured at $H = 7$ T (solid squares), and the extrapolated FM moment at $H = 0$ (open squares). Dashed lines are a guide to the eye.

ferromagnetism. A rough extrapolation to $T = 0$ suggests a saturated magnetic moment of $\sim 1 \mu_B/\text{Co}$ [Fig. 2(d)], which corresponds to a 1:1 mixture of low-spin (LS: t_{2g}^6, e_g^0 ; $S = 0$) and intermediate-spin (IS: t_{2g}^5, e_g^1 ; $S = 1$) states of Co^{3+} ions, if a simple FM spin order is realized. A similar conclusion, that Co^{3+} ions exhibit a 1:1 ratio of LS and IS states below the metal-insulator transition at $T \approx 360$ K [5,7,13], can be reached based on the Curie-Weiss fitting of the PM susceptibility in the temperature range 300–360 K [Fig. 1(b)]. It is worth noting that *polycrystalline* $\text{RBaCo}_2\text{O}_{5.5}$ samples demonstrate smaller FM moments [6–8], seemingly inconsistent with the expected Co spin states, which has been one of the mysteries of the FM state. The discovered Ising anisotropy, that prevents moments from being seen along the b and c axes, readily resolves this discrepancy.

To understand why Co^{3+} ions in $\text{GdBaCo}_2\text{O}_{5.5}$ even at zero temperature exhibit two different spin states, one should consider the oxygen ordering in $\text{GdO}_{0.5}$ planes, sketched in Fig. 3(a). The alternating filled and empty oxygen chains create two types of structural environment, octahedral and pyramidal, for Co ions; one of these environments stabilizes the LS ground state (t_{2g}^6, e_g^0 ; $S = 0$), while the other one makes the IS state (t_{2g}^5, e_g^1 ; $S = 1$) preferable. While our experiments can hardly distinguish whether the IS ground state is realized in pyramidal or octahedral positions, a structural study by Frontera *et al.* [13] suggests the IS state for Co ions in pyramidal sites. In this case, magnetic Co ions form 2-leg ladders extended along the a axis [black spheres in Fig. 3(a)] and separated by nonmagnetic layers.

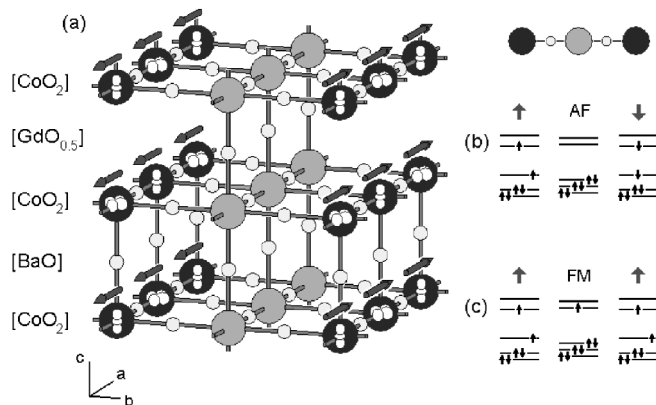


FIG. 3. (a) A sketch of the crystal and magnetic structure of $\text{GdBaCo}_2\text{O}_{5.5}$. Owing to the ordering of oxygen (small shaded spheres) into alternating empty and filled chains, the Co ions become nonequivalent and exhibit either an IS state (black spheres, where occupied $d_{3z^2-r^2}$ or $d_{x^2-y^2}$ e_g orbitals are shown), or a LS state (shaded spheres). Ba and Gd are omitted for clarity. (b) The b -axis interaction of IS- Co^{3+} ions mediated by LS- Co^{3+} results in AF ordering. (c) Excited (Co^{2+}) ions switch the b -axis interaction into the FM one.

The magnetic ordering in insulators is known to be predominantly caused by the superexchange (SE) interaction, whose sign for each pair of ions can be estimated using Goodenough-Kanamori rules [17]. The FM spin order in ladders can be explained by the orbital ordering among IS Co ions, an example of which is shown in Fig. 3(a). Owing to the reduced dimensionality (quasi-1D/2D) of the ladders, the FM order develops quite gradually upon cooling, being subject to strong fluctuations, as is evident in the $M(H)$ curves in Fig. 2(a). Eventually, FM-ordered ladders with spins aligned along the a axis are formed; however, whether a macroscopic magnetic moment will emerge or not depends on the relative orientation of moments between these ladders, which can be *only* ferro- or antiferromagnetic due to the Ising nature of the spins. Experimentally, the interaction between different FM ladders, mediated by spinless-Co-O layers [Fig. 3(b)], turns out to be antiferromagnetic, bringing about the AF ground state. Of course, our magnetization data cannot tell along exactly which axis, b or c , or both, the ladder stacking is AF, but this does not matter for the qualitative picture.

Quite naturally, the interladder coupling is weak, and switching from the ground-state AF order to the FM one can be induced by magnetic fields or temperature. To understand the role of temperature, one should consider the thermally excited states: upon heating, a certain amount of LS Co^{3+} ions become Co^{2+} , Co^{4+} , or change their spin state. Whatever the case, each excited ion acquires a nonzero spin and replaces the weak SE interaction between two IS Co ions on the neighboring ladders with usual SE interactions, providing a strong bridge between spin-ordered ladders [Fig. 3(c)]. Regardless of whether the excited spin couples ferro- or antiferromagnetically with the spins in ladders, the symmetry of the bridge makes it certain that the additional coupling between the ladders is FM. Therefore, thermally excited spins should inevitably induce an AF-FM transition at some temperature, if fluctuations will not kill the FM order in the ladders first. It is worth noting also that the AF ordering can be suppressed not only by magnetic fields or thermal excitations, but by changing the oxygen stoichiometry as well: any deviation from $x = 0.5$ also introduces Co^{2+} or Co^{4+} ions and should shift the AF-FM phase to lower temperature, which we have indeed observed experimentally [14].

To complete the picture of magnetic ordering in $\text{GdBaCo}_2\text{O}_{5.5}$, it is useful to estimate the scale of different magnetic interactions. The strongest one is definitely the FM superexchange between IS Co^{3+} ions within ladders, which can be estimated from the Curie temperature T_c : The molecular-field theory for 3D systems would give $J/k_B \sim 150$ K for $T_c = 300$ K; however, for the quasi-1D/2D magnetic ordering, J should be roughly twice as large [18]. The weak AF coupling between adjacent FM ladders, J_w , can be directly evaluated

from the critical field of the AF-FM transition: J_w/k_B reaches ~ 15 K at $T = 0$, where $H_c \sim 20$ T [Fig. 2(c)]. In fact, it is this weak AF coupling that makes possible the competition and easy switching between the AF and FM orders in $\text{GdBaCo}_2\text{O}_{5.5}$. Last, based on the magnetization anisotropy in the FM or AF state, we can estimate the spin anisotropy energy, which appears to be unusually large: The rotation of a spin from the spin-easy a axis to the b axis requires $\Delta E_{a-b}/k_B \sim 15\text{--}20$ K at $T = 260$ K, which grows up to $\sim 80\text{--}100$ K at $T = 2$ K; the energy necessary to turn a spin along the c axis seems to be at least 2 times larger. Thus, the spin anisotropy energy appears to be about 10 times larger than J_w , which explains the observed Ising-like behavior: the magnetic fields capable of inducing the AF-FM transition are still too weak to rotate the spins away from the a axis.

One might wonder how the reorientation of weakly coupled ladders affects the charge transport, bringing about a giant magnetoresistance. The MR mechanism may be quite simple: $\text{GdBaCo}_2\text{O}_{5.5}$ appears to be a narrow-gap insulator, where the carrier generation goes through the formation of $\text{Co}^{2+}\text{--Co}^{4+}$ pairs, and the excitation energy for these states may well depend on the magnetic order. Indeed, in a low-spin Co-O layer ($\parallel ac$), each thermally excited state strongly couples with two adjacent spin-ordered ladders, providing them with a FM bridge; correspondingly, if the ladders' moments are AF oriented, the resulting frustration should increase the energy of the excited state by $\sim 2J$. Thus, the relative ordering of adjacent FM ladders is capable of significantly changing the insulating-gap size. Applied magnetic fields align the FM ladders and reduce the insulating gap, which results in steplike increase in the number of carriers and decrease in resistivity [Fig. 4(a)]. Figure 4(b) demonstrates that the activation energy is actually diminished by the magnetic field, and thus the MR grows roughly exponentially upon decreasing temperature.

Two salient points should be emphasized in the MR behavior. The first one is the cooperative nature of the MR, whereby an apparently small energy of the magnetic field $g\mu_B H/k_B$, \sim several K, is capable of changing the carriers' activation energy by several hundreds K. The second point is the extremely large MR anisotropy: the 14-T field $H \parallel c$ can do nothing comparable to the MR caused by $H \parallel a$ [Fig. 4(c)], which confirms the remarkable Ising-like spin anisotropy, which could be overcome only by magnetic fields in the 100-T range.

The revealed Ising-like spin behavior together with the absence of significant structural disorder turns $\text{RBaCo}_2\text{O}_{5.5}$ into a model system for studying the competing magnetic interactions and accompanying MR phenomena. Moreover, $\text{RBaCo}_2\text{O}_{5.5}$ compounds may represent an intriguing realization of a new MR scheme — a kind of “magnetic field-effect transistor”—where the charge-carrier injection into a 2D semiconducting chan-

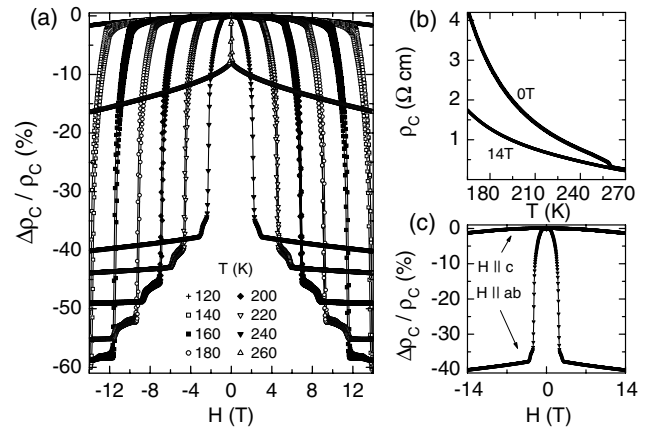


FIG. 4. c -axis MR of a twinned $\text{GdBaCo}_2\text{O}_{5.5}$ crystal. (a) $\Delta\rho_c/\rho_c$ measured at several temperatures for $H \parallel ab$. (b) T dependence of ρ_c at $H = 0$ and 14 T applied along the ab plane. (c) $\Delta\rho_c/\rho_c$ measured at $T = 240$ K for $H \parallel ab$ and $H \parallel c$.

nel is controlled by a magnetic state of neighboring “ligands.”

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