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Magnetic properties of perovskite-derived air-synthesized RBaCo$_2$O$_{5+\delta}$ (R=La—Ho) compounds

S. Roy,[1,2,*] I. S. Dubenko,[2,3] M. Khan,[2] E. M. Condon,[2] J. Craig,[2] and N. Ali[2]
[1]*Department of Physics, University of California San Diego, La Jolla, California 92093, USA*
[2]*Department of Physics, Southern Illinois University, Carbondale, Illinois 62901-4401, USA*
[3]*Canadian Light Source, University of Saskatchewan, Saskatoon, Canada S7N 0X4*

W. Liu and B. S. Mitchell
Department of Chemical Engineering, Tulane University, New Orleans, Louisiana 70118, USA
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A detailed magnetic study has been carried out for the air-synthesized RBaCo$_2$O$_{5+\delta}$ (R=La—Ho) cobaltites. RBaCo$_2$O$_{5+\delta}$ compounds exhibit complex magnetic behavior depending on the rare earth, the oxygen content, and variable Co valency. Spin-state transitions have been observed in the paramagnetic region at $T \approx 350$ K for R=Nd, Sm, Eu, Gd, and Tb compounds. The spin transition was found to depend delicately on the oxygen content and can be detected at oxygen concentrations varied within 5.3–5.5. Clear effects of the rare earths on the magnetic properties of the compounds at low temperature have been observed. RBaCo$_2$O$_{5+\delta}$ compounds show Co weak ferromagnetism plus rare-earth paramagnetism for the heavy rare-earth-based compounds (Gd—Ho) and strongly ordered noncollinear ferromagnetic structure with high coercivity for light rare-earth-based compounds (Pr—Eu), thereby indicating the existence of a competing ferromagnetic and antiferromagnetic interaction at low temperatures. We show that the spin-state transition and low-temperature magnetic behavior have two distinct sources of origin. A phenomenological model incorporating the effects of rare-earth and Co—O interactions has been proposed to explain the low-temperature magnetic behavior of the RBaCo$_2$O$_{5+\delta}$ compounds.

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I. INTRODUCTION

The discovery of technologically important magnetoresistive materials, in particular the manganites, has resulted in renewed extensive studies of other magnetoresistive oxide materials like cobaltites.[1] Studies of La$_{1-x}$Sr$_x$CoO$_3$ show that the compound is metallic for $x=0.25$ although the magnetoresistance (MR) ratio is low compared to manganite.[2] However, subtle changes in the composition leading to RBaCo$_2$O$_{5+\delta}$ (R=Eu and Gd) have been reported to exhibit a higher MR ratio.[3] These compounds of the general formula RBaCo$_2$O$_{5+\delta}$ are layered perovskites with alternating Co—O square pyramid and octahedral layers along the b axis. Depending on the oxygen content there is a variation in the mean oxidation number of cobalt. The change in the number of Co ions of different oxidation number due to difference in oxygen content of the sample results in a variation of the structure as well as magnetic and electrical transport properties. Moreover, Co has the ability to exist in different spin states, and a temperature- induced low-spin (LS) state Co^{3+} ($t_{2g}^6, S=0$) to high-spin (HS) state Co^{3+} ($t_{2g}{}^4 e_g{}^2, S=2$) transition in LaCoO$_3$ has been observed.[2,4] Therefore, in addition to the interplay of structure, magnetic, and electrical transport properties, there exists another degree of freedom—namely, the spin state of the Co ion—that needs to be taken into account for understanding the properties of this system.

For the stoichiometric compound RBaCo$_2$O$_5$ ($\delta=0$), the Co^{2+}/Co^{3+} ratio is unity and the Co—O forms a square pyramidlike structure with the rare earth (R) and Ba being arranged alternately along the c axis.[3,5–8] On the other hand, for RBaCo$_2$O$_6$ ($\delta=1$), the Co^{3+}/Co^{4+} ratio is unity and the Co—O octahedral structure is realized. The only reported compound of the above formula is LaBaCo$_2$O$_6$, which has a simple cubic perovskite structure with a single mixed La/Ba site.[9] The intermediate case (and the interesting one) is RBaCo$_2$O$_{5.5}$, ($\delta=0.5$) where the structure gets quite complicated with the coexistence of both Co—O square pyramid and Co—O octahedra.[7,10] The magnetic properties have also been found to be strongly oxygen content dependent. Thus, whereas GdBaCo$_2$O$_{5.45}$ shows a complicated magnetic behavior with possible spin-state transitions, GdBaCo$_2$O$_{5.0}$ shows no such complexity.[11,12] Similar oxygen-content-dependent changes in properties have also been observed in NdBaCo$_2$O$_{5+\delta}$.[13,22] A high-magnetic-field study of GdBaCo$_2$O$_{5.45}$ shows the presence of a first-order field-induced transition below the Néel temperature of 255 K which is attributed to the polarization of Gd and Co moments.[14] A neutron diffraction study of TbBaCo$_2$O$_{5.4}$ indicates that in the intermediate-spin state the Co ions are ordered antiferromagnetically in addition to a spin reorientation process.[15] Theoretical studies of YBaCo$_2$O$_5$ by Kwon *et al.*[16] indicate that Co^{2+} and Co^{3+} are in two different spin states and the orbital moment contributes significantly to the net magnetic moment. On the other hand, local density approximation (LDA) calculations on TbBaCo$_2$O$_{5.5}$ by Wu show that Co^{3+} is in a high-spin state with competition between the high-spin superexchange antiferromagnetic (AF) coupling and double-exchange ferromagnetic (FM) interaction being responsible for complex magnetic properties.[17] It is clear, therefore, that there is a lot of information, but at the same time there is also a lack of coherency. In particular, the low-temperature behavior and role of rare earths is not clear at all. It is also not understood why subtle changes in oxygen would cause the compound to show drastic changes in magnetic properties.[11–13] Reports of systematic studies involving all the rare earths are very limited and until now to the best of our knowledge there is only one report by Maignan *et al.*[18] Since the overlap between the transition-metal *d* orbital and oxygen 2*p* orbital is strongly influenced by the average radius of ions on the *R* site, a systematic variation of the *R*-site cation size by varying the lanthanide will shed light on the role of the *d*-2*p* interaction in determining the magnetic properties and the effect of the rare earth itself. In this article we report on the result of our detailed study of the magnetic properties of air-synthesized $R\mathrm{BaCo_2O_{5+\delta}}$ (R=La—Ho) compounds. Various parameters like the paramagnetic Curie temperature and effective paramagnetic moment have been extracted from magnetization data to determine the spin-state transition and effect of the rare earth. A phenomenological model has been proposed to explain the low-temperature magnetic behavior of the $R\mathrm{BaCo_2O_{5+\delta}}$ compounds.

II. EXPERIMENTAL PROCEDURE

Ceramic polycrystalline samples of $R\mathrm{BaCo_2O_{5+\delta}}$ (R=La—Ho) were prepared using the conventional solid-state reaction method. Stoichiometric amounts of $R_2\mathrm{O}_3$, $\mathrm{BaCO_3}$, and CoO were thoroughly mixed and then calcined at 900 °C for 12 h. The calcined powder was then reground and sintered at 1000 °C for 15 h. The final step consisted of regrinding the aforementioned sintered powder, pressing into pellets and then sintering at 1100 °C for 24 h. The samples were cooled in the furnace by employing a cooling rate of 5 °C per minute. The sample quality was checked by x-ray diffraction (XRD) at room temperature. The XRD intensity data were collected by a Rigaku automated diffractometer with Cu $K\alpha$ radiation. The data were collected within the 2θ range of 20° and 100°, and refinement was done using the Rietveld powder diffraction profile fitting technique.[19] The oxygen content was determined using thermogravimetric analysis (TGA) (TA Instruments, Inc.) employing a platinum pan. Approximately 50–70 mg of sample was taken. The samples were heated from room temperature to 1000 °C at the rate of 10 °C per minute. The TGA was carried out with 95% Ar and 5% $\mathrm{H_2}$ at a pressure of 1 atm. Magnetization measurements were carried out by a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range 5–400 K. All the thermomagnetic data were taken after the samples were field cooled from room temperature to 5 K at 1 kG. The transition temperatures were determined from the maxima of the dM/dT versus temperature curves.

III. RESULTS

The oxygen content measurement shows that the oxygen content is different for different rare-earth-based compounds. This indicates a strong link between the *R*-site radius and the amount of oxygen that the compound can accommodate. The δ value for the end member of the $R\mathrm{BaCo_2O_{5+\delta}}$ series of compounds is approximately 0.2 while it increases to 0.5 for the intermediate compounds. The variation of the oxygen content is qualitatively similar to what has been reported in Ref. 18. However, as reported in Ref. 9, we did not see any evidence of oxygen being 6.0 in La-based compounds. The change in oxygen concentration results in a change in the oxidation number of Co ions. As a result a different ratio of the mixed-valence Co ions is realized. In case of the end members of the series ($\delta \approx 0.2$), the $\mathrm{Co^{3+}/Co^{2+}}$ ratio is smaller compared to the intermediate compounds, since the $\mathrm{Co^{2+}}$ number decreases as δ increases from 0 to 0.5. This change in the Co mixed-valency ratio has a dramatic effect on the magnetic properties as we will see later. The δ values

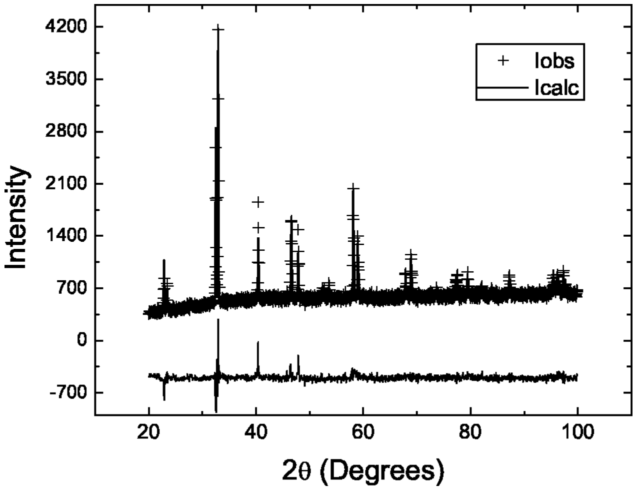

FIG. 1. XRD pattern of $\mathrm{NdBaCo_2O_{5.57}}$. The cross points are experimental data points. The fitted curve is superposed on it. The difference curve is shown at the bottom.

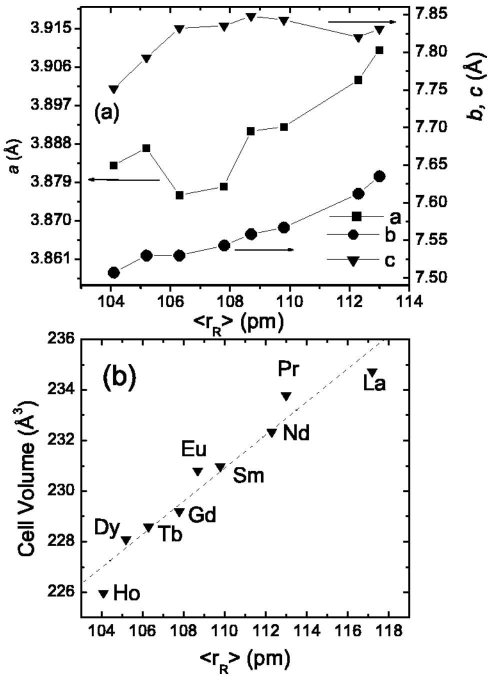

FIG. 2. Variation of the (a) lattice parameter and (b) unit cell volume with $\langle r_R \rangle$. The dashed line is a straight line fit to the cell volume data.

TABLE I. Lattice parameters and magnetic properties of $R\mathrm{BaCo_2O_{5+\delta}}$ compounds. The ionic radius is the radius of the R^{3+} ions. δ is the amount of oxygen excess of 5.0. a, b, and c are the lattice parameters. T_C, T_N, and T_ST are the Curie, Néel, and spin transition temperatures, respectively. θ is the Curie-Weiss constant. p_eff is the effective paramagnetic moment, and s and R_p are the goodness-of-fit factor and the residual factor as obtained from Rietveld refinement.

R^{3+} ions	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}
Ionic radius (pm)	117.2	113.0	112.3	109.8	108.7	107.8	106.3	105.2	104.1
δ	0.24(1)	0.53(1)	0.57(8)	0.39(4)	0.34(2)	0.43(3)	0.41(0)	0.20(8)	0.20(9)
a (Å)	3.886(1)	3.910(4)	3.903(8)	3.892(2)	3.891(7)	3.878(5)	3.877(4)	3.891(4)	3.883(9)
b (Å)	3.886(1)	7.830(6)	7.821(3)	7.842(7)	7.847(7)	7.836(4)	7.833(0)	7.770(6)	7.754(2)
c (Å)	3.886(1)	7.635(3)	7.612(6)	7.567(4)	7.558(7)	7.544(2)	7.533(4)	7.533(6)	7.508(7)
Cell volume (Å^3)	58.68	233.75	232.36	230.95	230.77	229.25	228.77	227.75	226.06
T_N (K)	—	76.5	107.9	221.7	236.5	242.9	254.1	188.6	178.2
T_C (K)	179.16	115.71	246.7	263.9	282.9	278.3	282.4	260.6	286.2
T_ST (K)	—	—	355.1	366.7	368.0	365.5	348.3	—	—
θ (K)	201.5	54.15	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	41.46	14.67
			215.05	283.62	182.35	205.98	217.24		
			$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$		
			44.82	94.19	260.27	175.08	33.78		
p_eff of R^{3+} ions (μ_B)	0	3.557	3.619	0.842	0	7.937	9.721	10.630	10.583
	4.122	5.311	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	$T<T_\mathrm{ST}$	9.803	9.281
			3.536	1.752	3.118	6.04	6.285		
p_eff of $R\mathrm{BaCo_2O_{5+\delta}}$ (μ_B)			$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$	$T>T_\mathrm{ST}$		
			5.265	5.265	6.063	8.99	9.89		
s	1.354	1.469	1.511	1.975	2.025	1.721	1.954	2.326	2.490
R_p	3.240	3.307	4.487	3.765	3.512	3.762	3.801	3.812	3.971

for the different compounds are given in Table I.

Room-temperature x-ray diffraction shows the formation of homogeneous single-phase compounds. Except for $\mathrm{LaBaCo_2O_{5+\delta}}$ all other compounds have an orthorhombic crystal structure with space group *Pmmm*. For $\mathrm{LaBaCo_2O_{5+\delta}}$, a simple cubic structure with space group *Pm*3*m* and lattice parameter of 3.886(1) Å is obtained. Figure 1 shows a typical XRD pattern for $\mathrm{NdBaCo_2O_{5.57}}$. The goodness of factors and residual factors as obtained for different compounds from Rietveld refinement is given in Table I. XRD refinement shows that for all the orthorhombic $R\mathrm{BaCo_2O_{5+\delta}}$ compounds, the lattice parameters may be expressed as $a\times 2a \times 2a$, which indicates the doubling of the lattice parameter along the b and c axes.[18] Figure 2 shows the variation of lattice parameters as function of the radius of R site $\langle r_R\rangle$. Both b and c axes increases with increasing R-site radius with the lattice parameter a, which shows a dip around $106 \leqslant \langle r_R\rangle \leqslant 109$ pm and then increases as $\langle r_R\rangle$ increases. The unit cell volume decreases monotonically with decreasing $\langle r_R\rangle$, and a straight line could be fitted reasonably well to the unit cell volume. This indicates that the cell volume decrease is due to the lanthanide contraction.

Figure 3 shows the temperature dependence of the magnetization $M(T)$ for $R\mathrm{BaCo_2O_{5+\delta}}$ compounds. The $M(T)$ of La-based compound [Fig. 3(a)] is typical for ferromagnetic ordering with $T_\mathrm{C}=179$ K. In contrast, the $R\mathrm{BaCo_2O_{5+\delta}}$ compounds with magnetic R ions do not show simple ferromagnetic behavior, but have a complicated magnetic property and they can be broadly divided into two groups as described below.

(i) The compounds with light rare earths (Pr–Eu) show basically similar $M(T)$ behavior. As shown in Fig. 3(b), with a decrease in temperature, $\mathrm{PrBaCo_2O_{5+\delta}}$ makes a paramagnetic to ferromagnetic transition with $T_\mathrm{C}=115$ K. The sharp decrease of magnetization below T_C indicates the likelihood of the presence of antiferromagnetic interactions in the compound. In the case of $\mathrm{NdBaCo_2O_{5+\delta}}$ two transitions have been observed at 107 and 246 K, respectively [Fig. 3(b)]. We attribute the transition at 246 K as due to cobalt ions but the origin of the first transition at $T_\mathrm{N}=107$ K is not very clear, although a different magnetic phase being the reason could not be ruled out.[20] Magnetization versus temperature curves for $R\mathrm{BaCo_2O_{5+\delta}}$, $R=$Sm, Eu, are shown in Fig. 3(c) and are in good agreement with previously published results.[3,21] The compounds pass through several magnetic states as the temperature is scanned from 5 K to 400 K. Near $T=250$ K, the magnetization increases steeply and the compound goes from an antiferromagnetic to a ferromagnetic state followed by a ferromagnetic-to-paramagnetic transition. The relevant transition temperatures are given in Table I. A nonzero magnetization until the lowest temperature of 5 K indicates that the compound is not fully antiferromagnetic but has a substantial ferromagnetic component. The coexistence of the antiferromagnetic-ferromagnetic phase at low temperatures will be more evident in field-dependent magnetization curves and will be discussed at length later.

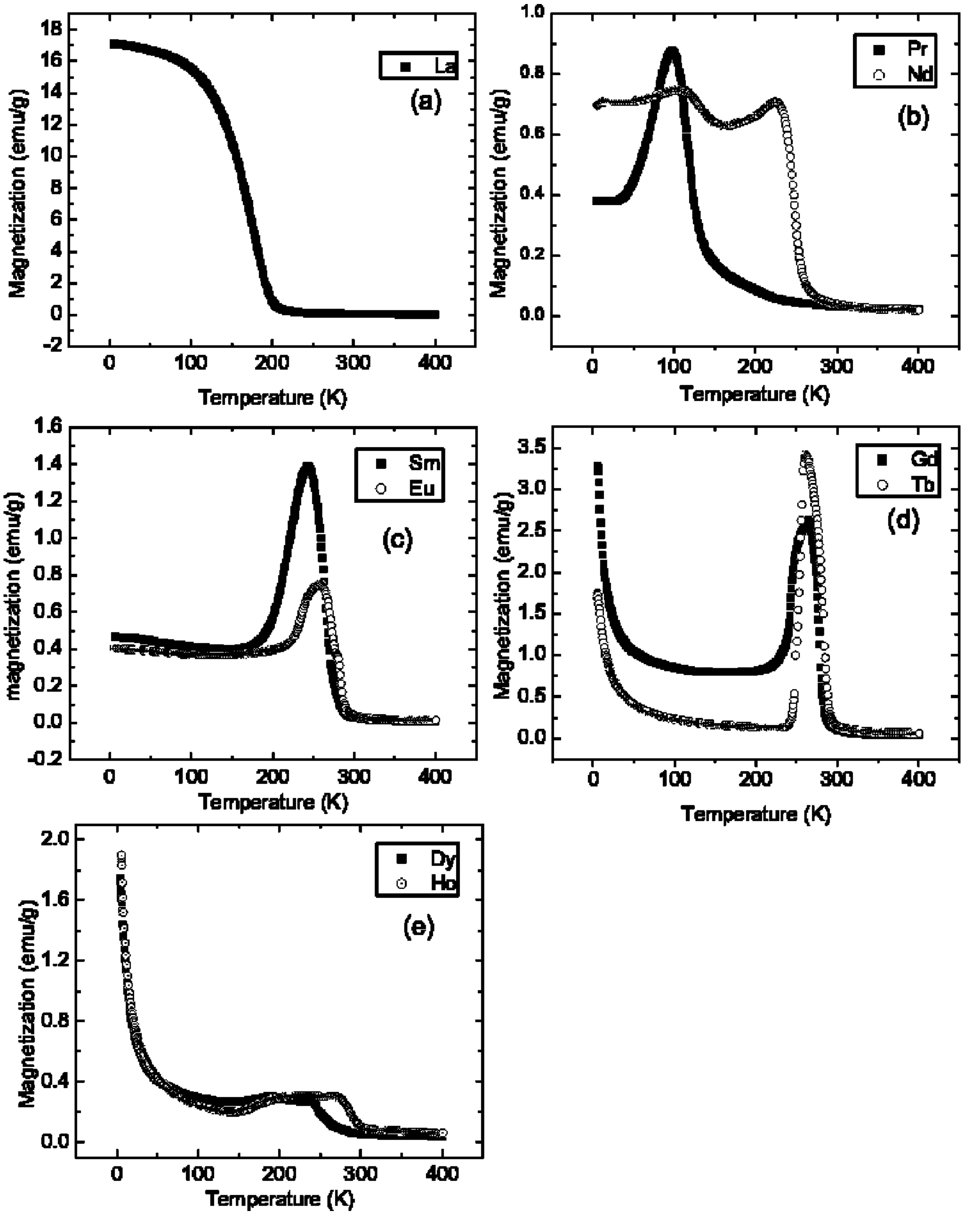

FIG. 3. Field-cooled magnetization versus temperature curves for $R\text{BaCo}_2\text{O}_{5+\delta}$ compounds (R =La—Ho).

(ii) For the heavy rare-earth-based $R\text{BaCo}_2\text{O}_{5+\delta}$ (R =Gd—Ho) compounds, the temperature-dependent magnetization shows paramagnetic behavior in the low-temperature region and weak ferromagnetism in the temperature range $190 \leqslant T \leqslant 260$ K, with an antiferromagnetic phase in between [Figs. 3(d) and 3(e)]. The effective paramagnetic moment is calculated as $8.52\mu_B$/f.u., $9.98\mu_B$/f.u., $10.34\mu_B$/f.u., and $10.66\mu_B$/f.u. for Gd-, Tb-, Dy-, and Ho-based compounds, respectively. Since these values are very near to the p_{eff} value of the free R^{3+} ion, it implies that at least for the heavy rare-earth-based $R\text{BaCo}_2\text{O}_{5+\delta}$ system, Co has negligibly small moment in the low-temperature region.

A magnetic anomaly in the high-temperature ($T \geqslant 310$ K) paramagnetic state has been observed for several of the intermediate lanthanides from Nd to Tb [Figs. 4(a)–4(e)]. The anomaly is manifested in the form of a decrease of slope in the thermomagnetization curve in the temperature range $355 \leqslant T \leqslant 370$ K. Resistivity and structure measurements have shown that coinciding with the slope change temperature there is structural phase transition and metal-insulator transition in these compounds.[10,18,22] The slope change means an increase in the effective paramagnetic moment of the compound. One of the likely causes for such an increase in the p_{eff} value could be a spin-state transition of the Co^{3+} ions. It may be noted that all the compounds that show the spin-state transition have oxygen content close to 5.5. It is also noted that neither the metal-insulator nor the high-temperature spin transition has been observed for the light (La, Pr) and heavy (Dy, Ho) rare-earth-based compounds although the entire series of $R\text{BaCo}_2\text{O}_{5+\delta}$ compounds does exhibit a ferromagnetic-to-paramagnetic transition. The spin transition temperatures T_{ST} are listed in Table I.

The low-temperature magnetic state of the $R\text{BaCo}_2\text{O}_{5+\delta}$ compounds have been determined by measuring the magnetization as function of applied magnetic field at a temperature of 5 K. The results of the measurements are shown in Figs. 5(a)–5(f). The $M(H)$ curve for $\text{LaBaCo}_2\text{O}_{5+\delta}$ shows spontaneous irreversible magnetization that increases with field, in-

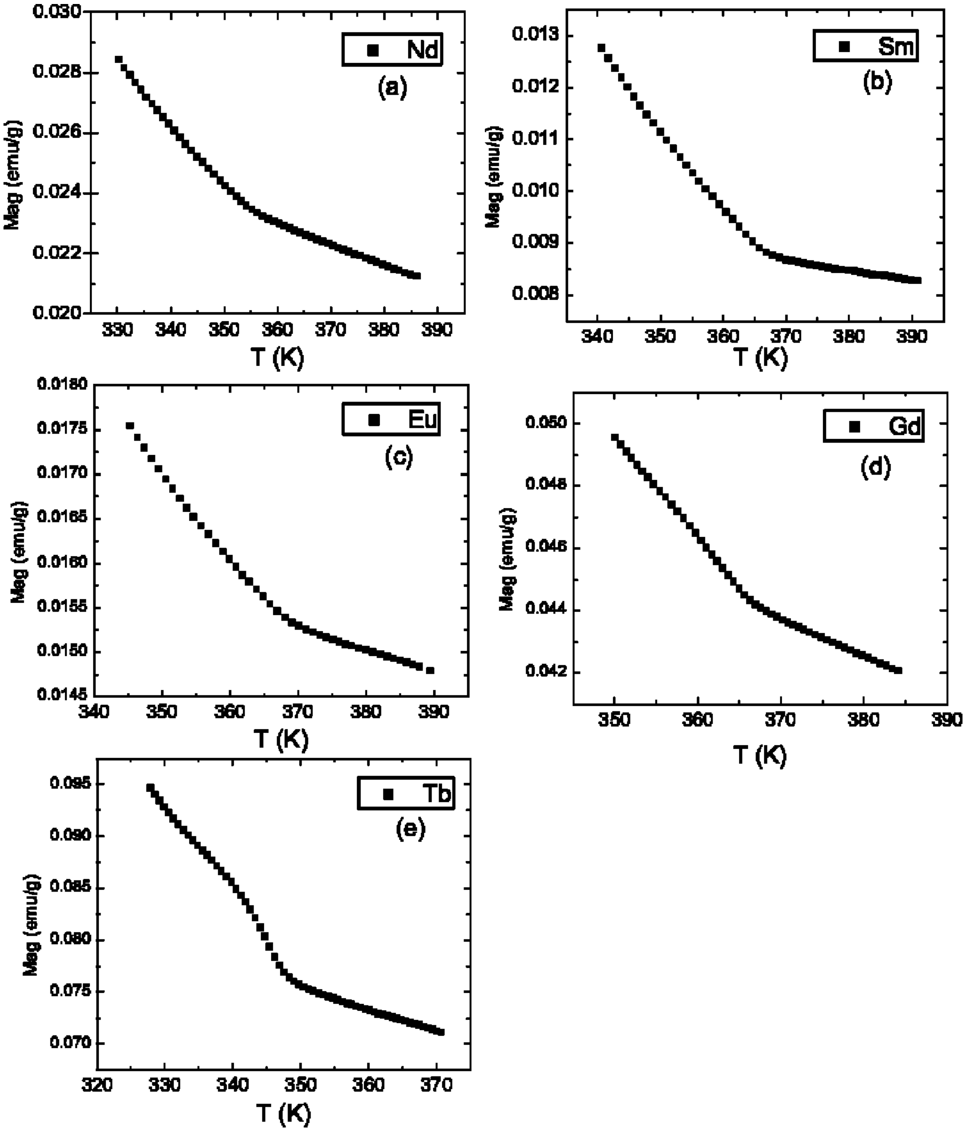

FIG. 4. Spin-state transition observed for $R\mathrm{BaCo_2O_{5+\delta}}$ compounds (R=Nd—Tb).

dicating the predominantly ferromagnetic nature of the compound. Since Co is the only magnetic species in $\mathrm{LaBaCo_2O_{5+\delta}}$, the ferromagnetism in the compound is due to the ferromagnetic alignment of the Co ions. As the field is increased, the spins become aligned, causing an increase in the magnetization. The magnetization at 5 K in a 5-T field is 36.85 emu/g, which agrees well with the published value.[20] The shape of the hysteresis curve for $R\mathrm{BaCo_2O_{5+\delta}}$, R =Pr—Eu is quite different [Figs. 5(b)–5(d)]. The magnetization value at 5 T is far less than for $\mathrm{LaBaCo_2O_{5+\delta}}$ and shows no sign of saturation. The $M(H)$ curves have a linearly increasing tendency as a function of applied magnetic field along with a considerable remanent magnetization. This is due to the presence of both antiferromagnetic and ferromagnetic interactions at low temperatures with the antiferromagnetic component being the larger of the two. For the remaining four compounds (Gd—Ho), the magnetization versus applied magnetic field shows a typical paramagnetic behavior. In accordance with a typical paramagnetic behavior, at zero applied magnetic field the spins are devoid of any ordering. As the applied field increases, the spins gradually become oriented towards the field and the magnetization increases. Note that the paramagnetic nature of the $R\mathrm{BaCo_2O_{5+\delta}}$, R=Gd—Ho, has also been observed in $M(T)$ curves at low temperatures. It is worth mentioning that results from both $M(T)$ and $M(H)$ curves show that, magnetically, the $R\mathrm{BaCo_2O_{5+\delta}}$ series of compounds can be divided into three groups. Namely, compounds with nonmagnetic R ions (La), light magnetic rare earths (Pr—Eu), and heavy magnetic rare earths (Gd—Tb).

IV. DISCUSSION

We start the discussion section by summarizing three important results that have emerged from our studies: (1) the coexistence of ferromagnetic and antiferromagnetic phases, (2) the existence of spin-state transition temperature T_{ST} for $R\mathrm{BaCo_2O_{5+\delta}}$ compounds with R=Nd, Sm, Eu, Gd, and Tb, and (3) radical changes in magnetic properties of the compound as we pass from light to heavy rare-earth compounds as is evident from $M(T)$ and $M(H)$ curves. To get a better understanding of the magnetic behavior of Co in different

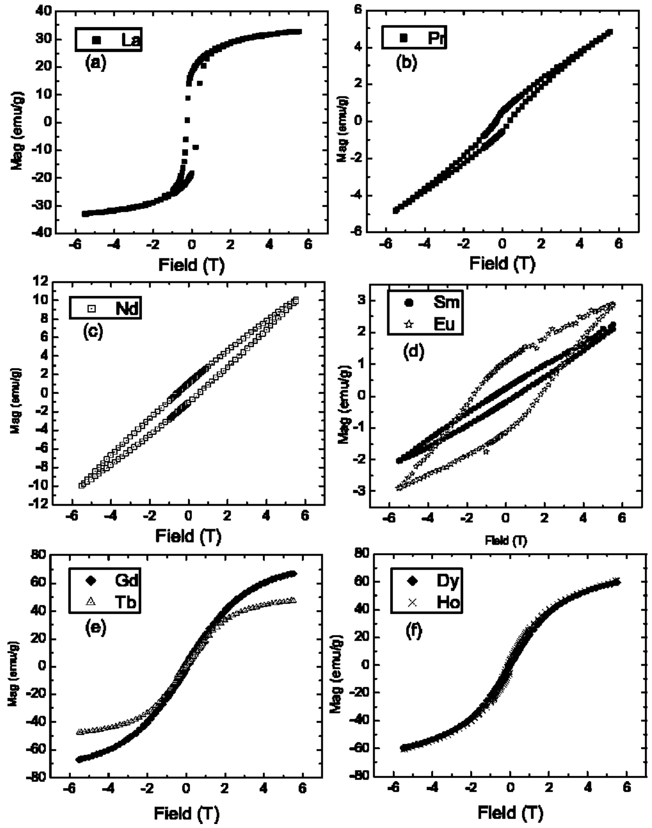

FIG. 5. Applied magnetic field dependence of magnetization at a temperature of 5 K of $R\mathrm{BaCo_2O_{5+\delta}}$ compounds (R=La—Ho).

electronic states, we have determined the Curie-Weiss constant θ and the effective magnetic moment p_{eff} for the spin-state transition exhibiting compounds in the two temperature regions of $T_{\mathrm{C}} < T < T_{\mathrm{ST}}$ and $T_{\mathrm{ST}} < T < 400$ K. In the case $T_{\mathrm{C}} < T < T_{\mathrm{ST}}$, the compounds have paramagnetic Co in the *intermediate*-spin state and paramagnetic rare earth, while for $T_{\mathrm{ST}} < T < 400$ K, Co is in *high*-spin state and paramagnetic rare earth. Since θ is related to exchange interaction characteristics, by determining θ below and above T_{ST}, information about exchange interaction is obtained for compounds with Co in different spin states. This is shown in Fig. 6 where the value of θ is plotted both below and above T_{ST} as a function of the rare-earth ion size of the spin transition exhibiting compounds. The θ remains positive for all the compounds for $T_{\mathrm{C}} < T < T_{\mathrm{ST}}$, whereas in case of $T_{\mathrm{ST}} < T < 400$ K, the θ changes sign and becomes negative for Sm-, Eu-, and Gd-based compounds and has substantially smaller value for Nd and Tb compounds. Thus, not only ferromagnetism and antiferromagnetism coexist in these compounds, the intermediate to high-spin transition of Co increases antiferromagnetism in spin transitions exhibiting compounds with $\mathrm{EuBaCo_2O_{5+\delta}}$ having maximum antiferromagnetism ($\theta = -277$ K).

The spin-state transition of Co from IS to HS is observed only for compounds with R=Nd, Sm, Eu, Gd, and Tb. p_{eff} of the above-mentioned rare-earth-based compounds show that its increase above T_{ST} is much larger than the corresponding value below T_{ST}. Such an increase can happen if Co makes a transition from the intermediate- to high-spin state. Further, we also find that all the spin transitions exhibiting compounds have oxygen content close to 5.5. An oxygen content of 5.5 means the presence of only $\mathrm{Co^{3+}}$ ions and the existence of alternate Co—O octahedral and square pyramidlike structures.[10,22] Therefore, it seems that instead of a mixed valency of the Co ions, it is the special structure of alternating octahedral and square pyramids at O=5.5 that drives the IS→HS spin-state transition. These facts are summarized in Fig. 7, where we have plotted the phase diagram of the $R\mathrm{BaCo_2O_{5+\delta}}$ series of compounds. Various parameters like T_{C}, T_{N}, and T_{ST} are plotted against the rare-earth radius and oxygen content. The shaded region in the $\langle r_R \rangle - \delta$ plane indicates the area that corresponds to the spin-state transition. We hypothesize that if the $\langle r_R \rangle$ and δ of a $R\mathrm{BaCo_2O_{5+\delta}}$ compound is such that it falls within the shaded area; then, the

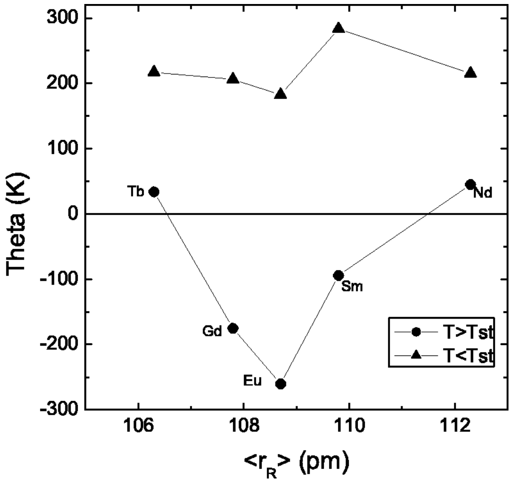

FIG. 6. Curie-Weiss constant plotted as a function of $\langle r_R \rangle$ in the temperature regions of $T_{\mathrm{C}} < T < T_{\mathrm{ST}}$ and $T_{\mathrm{ST}} < T < 400$ K for Nd-, Sm-, Eu-, Gd-, and Tb-based compounds.

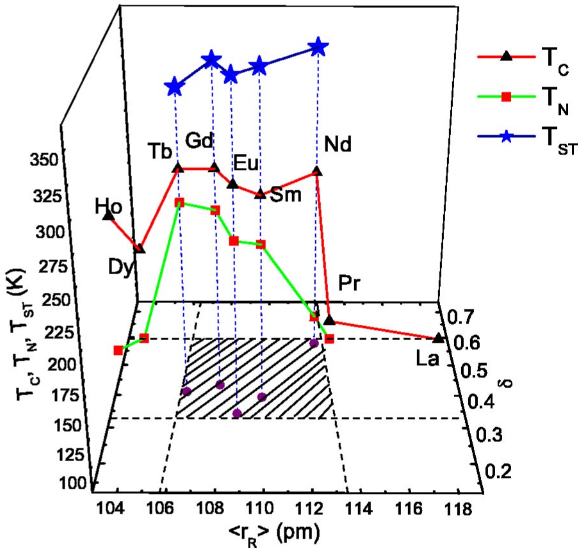

FIG. 7. (Color online) Phase diagram of $R\mathrm{BaCo_2O_{5+\delta}}$ compounds (R=La—Ho). T_C, T_N, and T_{ST} are plotted against the rare-earth radius and oxygen content. Vertical dotted lines are projections of T_{ST} onto the $\langle r_R \rangle$-δ plane.

Co IS-HS spin-state transition will be observed for that compound. This leads us to make the important conclusions: the IS→HS spin transition of Co is governed by the (1) oxygen content and (2) crystal cell volume.

An inspection of Fig. 5 indicates that the $R\mathrm{BaCo}_2\mathrm{O}_{5+\delta}$ compounds show Co weak ferromagnetism plus rare-earth paramagnetism for the heavy rare-earth-based compounds (Gd—Ho) and strongly ordered noncollinear ferromagnetic structure with high coercivity for light rare-earth-based compounds (Pr–Eu). We propose a model based on a phenomenological approach to explain the low-temperature magnetic behavior of the $R\mathrm{BaCo}_2\mathrm{O}_{5+\delta}$ compounds. At low temperature, a possible weak interaction of the rare earth with Co has been proposed.[23] Considering the existence of a nonnegligible *R*-Co interaction, the magnetic property of the $R\mathrm{BaCo}_2\mathrm{O}_{5+\delta}$ compounds then have contributions from a rare-earth magnetic subsystem and Co (oxygen is nonmagnetic) magnetic subsystem. We can then write $E_{\mathrm{xchange}}=E(R\text{-}R)+E(\mathrm{Co—Co})+E(R\text{-Co})$, where *R*-*R*, Co—Co, and *R*-Co are the rare-earth interaction, Co interaction, and rare earth–Co interaction and all these interactions are indirect. The Co magnetic subsystem has a noncollinear complicated magnetic structure with mutually orthogonal noncompensating weak ferromagnetic moment and antiferromagnetic order resulting in a net strong antiferromagnetic component below T_{C} (Ref. 10). Therefore the Co—Co interaction has two components: a positive component responsible for ferromagnetism and a negative component that gives rise to antiferromagnetism. The *R*-*R* interaction is weak. The *R*-Co interaction is positive for light rare-earth and negative for heavy rare-earth-based compounds.

For the heavy rare-earth-based compounds, the Co subsystem starts to get ordered below T_{C} and acts opposite to the *R*-*R* interaction and prevents the rare earth from getting ordered, resulting in paramagnetic rare earth. As temperature decreases, negative *R*-Co increases. The *R*-Co together with negative Co—Co interaction increases the effective magnetic field acting on the rare earth. This causes the *R* subsystem to order opposite the Co moments. The magnetization therefore decreases and an antiferromagneticlike transition is observed for Gd- and Tb-based compounds. The magnetic structure of the *R* subsystem is governed by the *R*-Co interaction. Also, the antiferromagnetic transition at T_{N} is induced by Co via the *R*-Co interaction. At low temperatures, Co goes to a low-spin state. The Co moment and *R*-Co interaction now have a diminished value. Hence, although the *R*-*R* interaction increases, the overall effective field acting on the *R*-*R* subsystem is not big enough, thereby resulting in a paramagnetic or almost paramagnetic behavior of the heavy rare earth at low temperatures, as experimentally observed. It might be noted that the difference between the Gd, Tb, Dy, and Ho compounds, as far as low temperature is concerned, is in the magnitude of the *R*-Co exchange term. The value of effective magnetic field originated by the Co subsystem and acting on the *R* subsystem depends on the Co moment and constants of the *R*-Co exchange field. They can have a maximum value for Gd and Tb, compared to Dy and Ho. As a result the effective field to create order in rare-earth magnetic subsystems is much smaller in Dy and Ho. This explains the small antiferromagnetic component seen in the Dy- and Ho-based compound [see Figs. 3(d) and 3(e)].

In the case of light rare-earth systems the *R*-*d* interaction changes sign because of a change in the sign of *L*-*S* coupling as governed by Hund's rule. Notice that this does not affect the antiferromagnetic Co magnetic subsystem because, for antiferromagnetic Co, the sign of the *R*-Co interaction does not matter. However, what does is the increase the ferromagnetic component of the Co subsystem. So we have now a high-anisotropy noncollinear ferromagnet as observed [Figs. 5(c) and 5(d)]. An additional contribution to the high coercivity could be the large anisotropy arising out of the 4*f* shells of the rare earth. It is worth mentioning that within this approach we can also explain the different magnetic behavior of $\mathrm{GdBaCo}_2\mathrm{O}_5$ and $\mathrm{GdBaCo}_2\mathrm{O}_{5.5}$. Because of the oxygen content, if the Co remains in the low-spin state throughout for $\mathrm{GdBaCo}_2\mathrm{O}_5$, then the paramagnetic state of $\mathrm{GdBaCo}_2\mathrm{O}_5$ is evident because of the very small *R*-Co interaction. The complex magnetic behavior of $\mathrm{GdBaCo}_2\mathrm{O}_{5.5}$ is already explained above. In this model, the Co behavior is sort of the same for all the whole series. The difference is in the effective field created by the *R*-Co interaction due to different magnetic *R* ions. It is this effective field acting on the Co subsystem that gives rise to antiferromagnetism for heavy rare-earth- (negative *R*-Co interaction) and ferromagnetism for light rare-earth- (positive *R*-Co interaction) based compounds at low temperature.

In conclusion, we have done a detailed study of the magnetic properties of the $R\mathrm{BaCo}_2\mathrm{O}_{5+\delta}$ ($R=$rare earth) family of compounds. We showed that the electronic transition of Co from the intermediate- to high-spin state and the low-temperature magnetic state of the system have different sources of origin. The Co spin-state transition is due to oxygen content in the compound. The spin-state transition can therefore be manipulated by varying the oxygen content in the system. The low-temperature magnetic state does not depend on the oxygen content but rather could be explained by considering the net interaction arising out of the rare-earth and Co magnetic subsystem. We have proposed a model which could explain reasonably well the low-temperature magnetic behavior of the $R\mathrm{BaCo}_2\mathrm{O}_{5+\delta}$ compounds.

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*Corresponding author. Email address: sujoy@physics.ucsd.edu

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