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Magnetic interactions in Cu-based layered transition metal oxides

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The nuclear and magnetic structures of several layered mixed copper-transition-metal oxides have been determined from neutron powder diffraction. The nuclear structures of the compounds studied here all consist of apex-linked pyramidal Cu/M-O_5 double layers separated by other structural blocks. These compounds were found to order antiferromagnetically within the Cu/MO planes, but along the apical direction ferromagnetic order occurs provided that the Cu/M ratio is close to unity. The magnetic order can be successfully explained by the electron configuration of the magnetic ions in the compounds: Cu$d_{z^2}^2 -$O2$p_z -$Fe/Co$d_{z^2}^1$ interaction favors ferromagnetic ordering along c while $d_{x^2-y^2}^1$-O$p_{x,y}$-$d_{x^2-y^2}^1$ superexchange results in antiferromagnetic order within the MO planes. In this context, it is found that the above explanation is consistent with the reported magnetic structures of all mixed Cu/Fe or Cu/Co compounds with layered structures.

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I. INTRODUCTION

Magnetic interactions in transition-metal (TM) oxides have attracted great attention in studies of high-T_c superconductivity and the giant magnetoresitance (GMR) effect in those materials. Doping of magnetic ions into the cuprates was carried out soon after the first observation of high-T_c superconductivity in order to investigate the interplay of magnetism and superconductivity. In the manganate systems, it is generally accepted that the e_g^1-O2p-e_g^0 double exchange interaction plays a vital role in the GMR effect. The common feature of these two systems is that their structures are composed of blocks of Cu-O or Mn-O planes separated by other structural building blocks. Different types of magnetic interactions between two transition-metal ions bridged by an anion (oxygen, halogen ions) have long been proposed, and can be rationalized by the Goodenough-Kanamori-Anderson (GKA) rules.[1–3] In the study of the aforementioned layered compounds, although application of the GKA rules has been used to successfully explain the interaction between the cations in the MO plane, little attention has been paid to interactions in the third dimension (perpendicular to the MO plane). Recently, we have found that in one of the Cu/Fe mixed layered oxides, $Y_2SrCuFeO_{6.5}$, a ferromagnetic (FM) interaction occurs between Cu-O-Fe along the apical bond direction.[4] We have proposed that this FM component can originate from a double exchange related interaction involving the $d_{z^2}^2 -$O2$p_z - d_{z^2}^1$ configuration. Similar Cu-O-Fe linkages can be found in many other layered cuprates, e.g., RBaCuFeO$_5$,RBaCuCoO$_5$, and RSrCuFeO$_5$ (R=rare earth elements),[5–7] where similar FM interaction through the apical oxygen is expected. However, the magnetic structures of the latter compounds can not be unambiguously determined because of the regular separation of the Cu/M ions by $\frac{1}{4}c$ along [001]. For this situation, the model with a FM interaction through the apical oxygen is indistinguishable from one with FM interaction through the oxygen free Y layer. Confirmation of such Cu$d_{z^2}^2 -$O2$p_z -$Fe$d_{z^2}^1$ FM ordering may be helpful for the rational design of new FM oxides where both inplane and out of plane FM interactions are needed. In order to further explore the existence of this type of FM interaction, we have studied four new samples which have a similar Cu-O-M linkage but do not suffer from the ambiguity caused by equal separation of magnetic ions along c. The predicted FM interaction has been observed and the results are reported below.

II. EXPERIMENTAL

The preparation of $Pb_2BaCuFeO_5X$(X=Cl, Br) has been reported previously.[8] Samples of $NdCeBaCuFeO_7$ and $NdCeBaCu_{0.9}Co_{1.1}O_7$ were prepared by sintering the corresponding oxides or carbonate up to 110 °C with several intermediate heatings. The samples were checked for their purity by x-ray diffraction with a Siemens D5000 diffractometer. Time of flight neutron powder diffraction (NPD) data of the compounds were collected at POLARIS (ISIS, RAL, Oxford, UK). Structure refinements were performed using the NPD data and the GSAS package.[9] In all the refinements, both the high resolution C bank (back scattering, $2\theta = 145°$) and the wide range A bank ($2\theta = 35°$) were used simultaneously.

III. RESULTS AND DISCUSSION

The four compounds studied belong to two different structural classes, i.e., $NdCeBaCu_{0.9}Co_{1.1}O_7$ and

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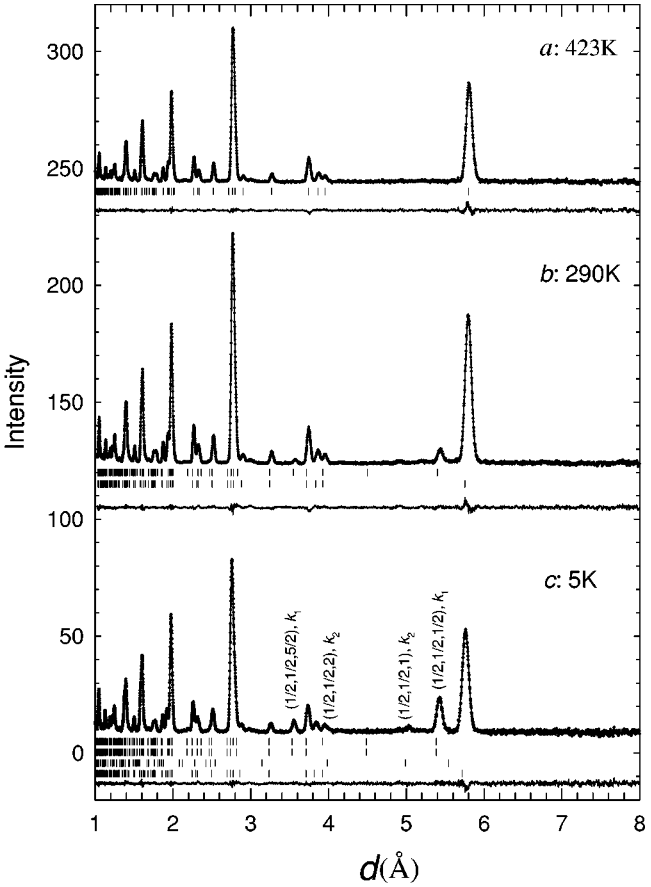

FIG. 1. Neutron diffraction patterns (*A* bank) of $Pb_2BaCuFeO_5Br$ at 423 K (top), 290 K (middle), and 5 K (bottom). The dots are observed data, lines are calculated and difference plots and the vertical marks represent the allowed diffraction peaks. [In panel (b), the first line of the vertical marks represent the magnetic reflections from the model of Figs. 3(a) and the second line represent nuclear only reflections. In panel (c) vertical marks from top to bottom represent the diffraction positions of the magnetic structural models of (a), (b), and (c) as shown in Fig. 3 and the nuclear only reflections].

$NdCeBaCuFeO_7$ are isostructural, as are $Pb_2BaCuFeO_5Cl$ and $Pb_2BaCuFeO_5Br$. The two structure types are, for convenience, considered separately.

A. Magnetic structures of $Pb_2BaCuFeO_5Cl$ and $Pb_2BaCuFeO_5Br$

The basic structure of these two compounds was reported by one of the present authors,[8] and consists of alternating oxygen deficient perovskite $BaCuFeO_5$ slabs and CsCl type Pb_2X slabs. In the perovskite slab, Cu and Fe are coordinated to five oxygen atoms forming Cu/FeO_5 pyramids. The CuO_5 and FeO_5 pyramids are joined together by sharing the apical oxygen atoms to form the double perovskite layer. This feature in the perovskite slab is common to the compounds studied here and in all of the related compounds mentioned in this report. Refinements of the nuclear structure using NPD data were straightforward and were in accordance with the model derived from the XRD study.[8] Models with possible Cu/Fe ordering and mixing of the Ba/Pb ions revealed no clear evidence of Fe/Cu ordering and only 4% intermixing of the Pb and Ba ions. During the refinements, we noticed that the temperature factor of the apical oxygen O1 in the perovskite slab was much bigger than those of the other ions at all temperatures for both the chloride and bromide phases. A splitting of its position reduced the temperature factor and improved the fit, e.g., for $Pb_2BaCuFeO_5Br$, with the splitting of O1, U_{iso}(O1) drops from 0.0134 Å^2 (RT, $\chi^2=6.13$) and 0.0089 Å^2 (5 K, $\chi^2=3.76$) to 0.0104 Å^2 (RT, $\chi^2=5.95$) and 0.0065 Å^2 (5 K, $\chi^2=3.64$). The ideal model with split O1 positions was then adopted in subsequent refinements.

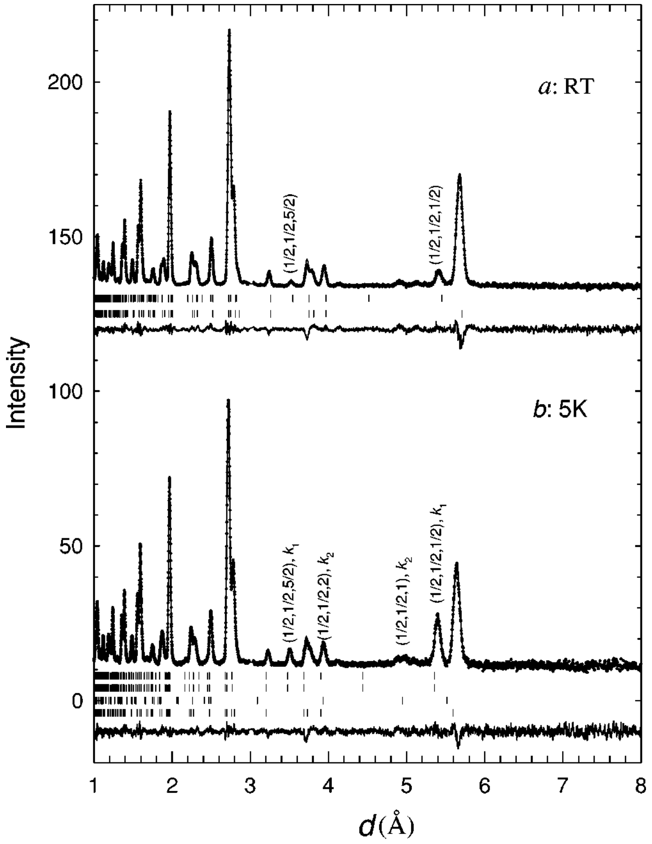

FIG. 2. Neutron diffraction patterns (*A* bank) of $Pb_2BaCuFeO_5Cl$ at room temperature and 5 K. The marks follow the same style as in Fig. 1.

At room temperature (RT, 290 K) and 5 K, additional peaks were observed for both compounds (Figs. 1,2) and are inconsistent with the nuclear model. A variable temperature NPD scan (Fig. 1) of $Pb_2BaCuFeO_5Br$ showed that the peaks disappeared above 150 °C and thus were magnetic in origin. All the magnetic peaks can be indexed as $(\frac{1}{2},\frac{1}{2},l/2,l=\text{odd})$ and $(\frac{1}{2},\frac{1}{2},l)$. For constructing a simple colinear magnetic structure, the first group of peaks needs the cell parameter c to be doubled and suggests a propagation vector of $k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, whereas the second group has a propagation vector $k_2=(\frac{1}{2},\frac{1}{2},0)$, and c remains the same as the nuclear cell. Furthermore, in the NPD patterns of both compounds, the second group of peaks becomes apparent only at 5 K. Mag-

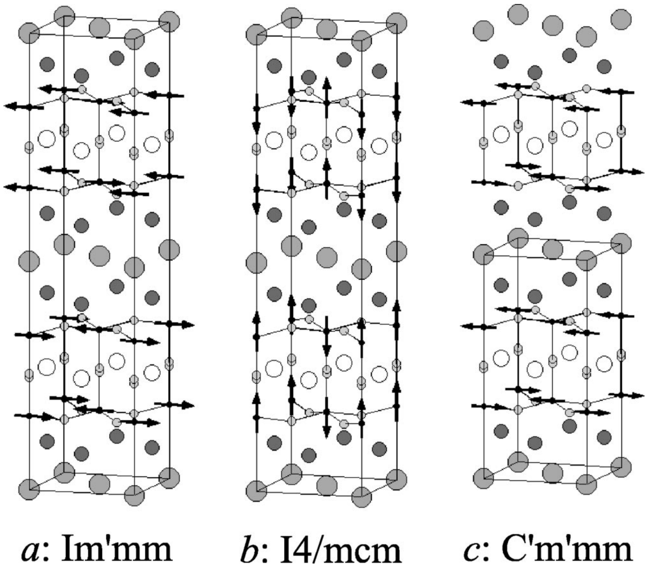
a: Im'mm *b*: I4/mcm *c*: C'm'mm

FIG. 3. Crystal and the three components of the magnetic structures of $Pb_2BaCuFeO_5X(X=Cl, Br)$. The large shaded circles represent Cl or Br atoms, the large open circles are Ba atoms, medium filled circles are Pb, small filled circles are Cu/Fe and small shaded circles are oxygen atoms. Magnetic unit cells are also shown in the figures.

netic structures with different moment alignments were tested. We found that for the k_1 component, models with FM ordering across the apical oxygen in the double perovskite slab, and AFM ordering within the MO plane and between the slabs [Figs. 3(a),3(b)] gave good fits. However, close inspection of the calculated and observed patterns revealed that for a model with the moments aligned in the ab plane, the intensity of $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ was underestimated, whereas for the moment along c, $(\frac{1}{2},\frac{1}{2},\frac{5}{2})$ was underestimated. Therefore a canted spin model with the spin alignment at an angle θ to c was adopted, and this gave good agreement for both peaks. The refinements for the 5 K patterns resulted in $\theta=62°$ with components $m_y=1.65\mu_B$ and $m_z=0.86\mu_B$ for $Pb_2BaCuFeO_5Br$, and $\theta=65°$ with $m_y=1.75\mu_B$ and $m_z=0.82\mu_B$ for $Pb_2BaCuFeO_5Cl$. For the low temperature k_2 component, a similar magnetic structure to the k_1 component but with an AFM interaction across the double layer [Fig. 3(c)], gave a good fit to the magnetic peaks. Considering only the double perovskite slab $(BaCuFeO_5)$, the magnetic order is a C type for the k_1 component and a G type for the k_2 one. At room temperature, for both samples, the k_2 group of peaks is absent and it seems also that the m_z component is unnecessary to fit the k_1 group of peaks. The magnetic peaks are modeled very well with the structure shown in Fig. 3(a), which contains only inplane moments $(m_y=1.01\mu_B)$ and retains the FM interaction across the apical oxygen. The final refined results are listed in Table I.

Bearing in mind that the k_2 peaks are absent in the room temperature patterns and the previous magnetization measurement showed a broad maximum at 120 K,[8] we may attribute ordering at this temperature to an AFM transition. It now becomes clear that $Pb_2BaCuFeO_5X$ has a first AFM transition associated with an FM interaction across the double Cu/FeO_5 layer above room temperature and some residual moments provide a second transition at 120 K

TABLE I. Structural parameters of $Pb_2BaCuFeO_5X(X=Cl, Br)$.

		$Pb_2BaCuFeO_5Br$		$Pb_2BaCuFeO_5Cl$	
Atoms	sites	z	U_{iso} (Å^2)	z	U_{iso} (Å^2)
Pb	$0.5,0.5,z$	0.17260(4)	0.0090(1)	0.16538(8)	0.0095(2)
5K		0.17203(4)	0.0035(1)	0.16429(8)	0.0044(1)
Ba	0.5,0.5,0.5	0.5	0.0153(3)	0.5	0.0110(4)
		0.5	0.0062(2)	0.5	0.0059(3)
Cu/Fe	$0,0,z$	0.32369(5)	0.0059(1)	0.31976(9)	0.0063(2)
(at 5 K)		0.32300(6)	0.0036(1)	0.31964(8)	0.0045(2)
O1 [c]	$0,0,z$	0.5090(3)	0.0104(3)	0.5078(5)	0.0128(4)
		0.5087(3)	0.0065(2)	0.5085(4)	0.0078(3)
O2	$0.5,0,z$	0.29600(4)	0.0090(1)	0.29095(6)	0.0094(2)
		0.29542(4)	0.0053(1)	0.29014(6)	0.0057(1)
X	0,0,0	0	0.0103(2)	0	0.0148(3)
		0	0.0016(2)	0	0.0055(2)
Nuclear cell	$P4/mmm$	$a=3.94972(5)$ Å,	$c=11.5720(4)$ Å	$a=3.93509(8)$ Å,	$c=11.3331(7)$ Å
at 5 K	$P4/mmm$	$a=3.94385(5)$ Å,	$c=11.5080(4)$ Å	$a=3.92470(8)$ Å,	$c=11.2541(7)$ Å
Magnetic cell I [a]	$Im'mm$	$a_M=b_M=\sqrt{2}a,\ c_M=2c$	$m_y=1.01(3)\mu_B$		$m_y=0.99(4)\mu_B$
Magnetic cell I [b]	$Im'mm$	$a_M=b_M=\sqrt{2}a,c_M=2c$	$m_y=1.65(5)\mu_B$		$m_y=1.75(5)\mu_B$
Magnetic cell II [b]	$I4/mcm$	$a_M=\sqrt{2}a,c_M=2c$	$m_z=0.86(7)\mu_B$		$m_z=0.82(8)\mu_B$
Magnetic cell III [b]	$C'm'mm$	$a_M=b_M=\sqrt{2}a,c_M=c$	$m_y=0.67(5)\mu_B$		$m_y=0.55(6)\mu_B$
Goodness of fit		$R_{wp}=2.55\%$	$\chi^2=5.95$	$R_{wp}=3.18\%$	$\chi^2=9.80$
at 5 K		$R_{wp}=1.48\%$	$\chi^2=3.64$	$R_{wp}=1.89\%$	$\chi^2=5.97$

[a] Room temperature.

[b] 5 K (second line).

[c] Half occupied.

TABLE II. Structural parameters of $NdCeBaCuFeO_7$ and $NdCeBaCu_{0.9}Co_{1.1}O_7$.

		$NdCeBaCuFeO_7$		$NdCeBaCu_{0.9}Co_{1.1}O_7$	
Atoms	sites	z	U_{iso} (Å^2)	z	U_{iso} (Å^2)
Nd/Ce	0,0,z	0.18793(2)	0.0033(1)	0.18726(3)	0.0035(1)
5 K		0.18782(2)	0.0018(1)	0.18700(3)	0.0022(1)
Ba	0,0,0	0	0.0109(2)	0	0.0093(2)
		0	0.0066(2)	0	0.0052(2)
Cu/Fe/Co	0.5,0.5,z	0.09679(2)	0.0059(1)	0.10019(5)	0.0095(2)
(at 5 K)		0.09683(2)	0.0055(1)	0.10047(6)	0.0077(2)
O1	0.5,0.5,0	0	0.0113(2)	0	0.0152(3)
		0	0.0074(2)	0	0.0117(3)
O2	0.5,0,z	0.11355(2)	0.0097(1)	0.11271(3)	0.0092(1)
		0.11344(2)	0.0071(1)	0.11282(3)	0.0072(1)
O3	0.5,0,0.25	0.25	0.0099(1)	0.25	0.0092(1)
		0.25	0.0079(1)	0.25	0.0078(2)
Nuclear cell	$I4/mmm$	$a=3.90370(5)$ Å,	$c=20.9032(7)$ Å	$a=3.90438(5)$ Å,	$c=20.6909(9)$ Å
at 5 K	$I4/mmm$	$a=3.89462(5)$ Å,	$c=20.8245(6)$ Å	$a=3.89703(6)$ Å,	$c=20.628(1)$ Å
Magnetic cell RT [a]	$C'c'cm$	$a_M=b_M=\sqrt{2}a, c_M=c$			$m_z=0.56(5)\mu_B$
Magnetic cell 5 K [b]	$C'c'cm$	$a_M=b_M=\sqrt{2}a, c_M=c$			$m_z=0.88(5)\mu_B$
Magnetic Cell 5 K [b]	$C'c'c'm'$	$a_M=b_M=\sqrt{2}a, c_M=c$	$m_x=1.46(3)\mu_B$		
Goodness of fit		$R_{wp}=2.77\%$	$\chi^2=6.23$	$R_{wp}=2.39\%$	$\chi^2=3.69$
at 5 K		$R_{wp}=1.65\%$	$\chi^2=2.80$	$R_{wp}=1.40\%$	$\chi^2=1.92$

[a] Room temperature.

[b] 5 K (second line).

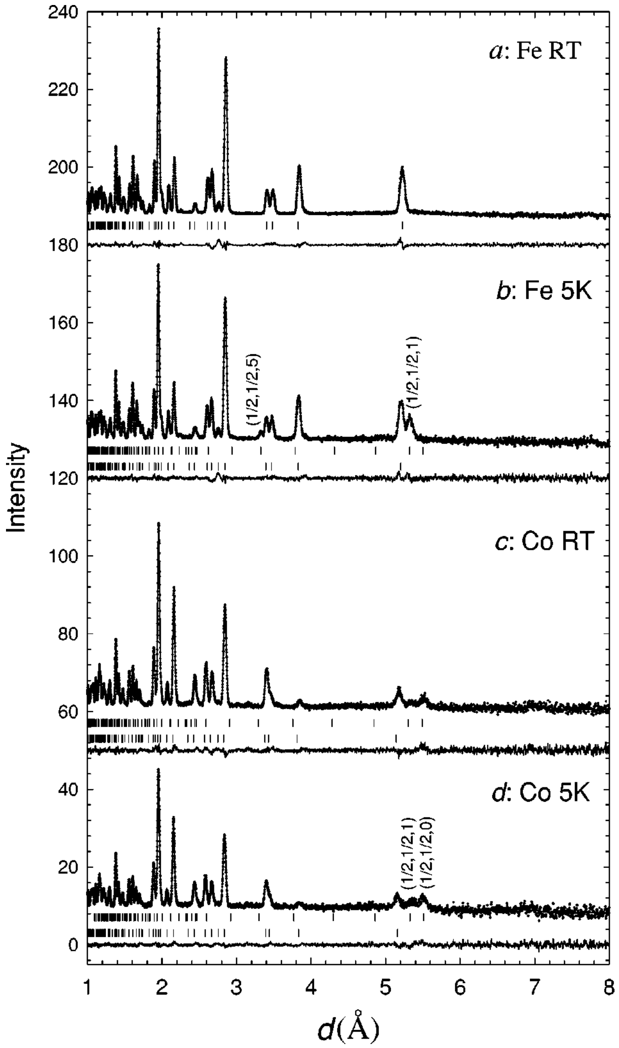

FIG. 4. Neutron diffraction patterns (*A* bank) of $NdCeBaCuFeO_7$ and $Nd,CeBaCu_{0.9}Co_{1.1}O_7$.

through the AFM interaction across the double layers. Similar two stage transitions have been implied by temperature dependent magnetization studies on $YBaCuFeO_5$ as reported by Caignaert *et al.*,[10] and more recently by Ruiz-Aragon *et al.*[11] The resultant overall ordered moments for the present Br and Cl containing compounds at 5 K are $1.98\mu_B$ and $2.01\mu_B$, and those at room temperature drop to $1.01\mu_B$ and $0.99\mu_B$, respectively. Although the moments are significantly lower than the ideal value ($3\mu_B$) for equal amounts of Cu^{2+}($1\mu_B$) and Fe^{3+}($5\mu_B$, high spin) ions, the refined values agree well with reported results on similar compounds,[4] where the reduction in moments is attributed to AFM fluctuation in the two-dimensional structures.

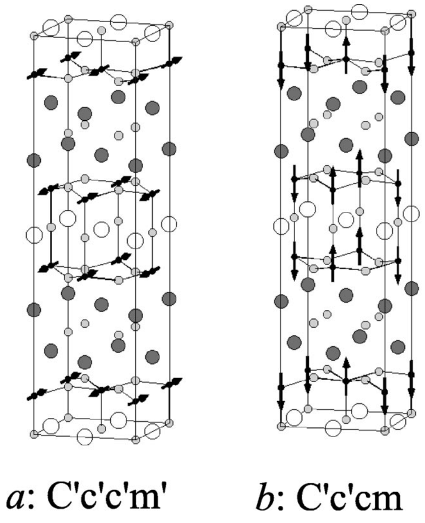
a: C'c'c'm' *b*: C'c'cm

FIG. 5. Crystal and magnetic structures of (a) $NdCeBaCuFeO_7$ and (b) $NdCeBaCu_{0.9}Co_{1.1}O_7$. The large open circles are Ba atoms, medium filled circles are Nd/Ce, small filled circles are Cu/Fe/Co and small shaded circles are oxygen atoms.

TABLE III. Magnetic structures of the compounds related to present study.

Case	Compounds	Prop. Vector	Moment(μ_B)	Temperature	Spin direction [a]	Reference
1	$Pb_2BaCuFeO_5Br$	$k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$1.65y+0.86z$	5 K	++PbPb−−	present
		$k_2=(\frac{1}{2},\frac{1}{2},0)$	$0.67y$	5 K	+−PbPb+−	
		k_1	$1.01y$	RT	++PbPb−−	
2	$Pb_2BaCuFeO_5Cl$	k_1	$1.75y+0.82z$	5 K	++PbPb−−	present
		k_2	$0.55y$	5 K	+−PbPb+−	
		k_1	$0.99y$	RT	++PbPb−−	
3	$YSrCuFeO_5$	k_1	$1.5z+0.2x$	2 K	++Y−−	7
		k_2	$1.6y$	2 K	+−Y+−	
4	$PrBaCuFeO_5$	k_1	$1.18z+0.7x$	2 K	++Y−−	13
		k_2	$1.53x$	2 K	+−Y+−	
5	$YBaCuFeO_5$	k_1	$1.32x+0.74z$	RT	++Y−−	10
		k_2	?	<200 K	+−Y+−	10
6	$YBaCuFeO_5$	k_1	$0.65x+1.46z$	RT	++Y−−	15
7	$YBaCuCoO_5$	k_1	$1.48z$	RT	++Y−−	16
8	$YBaCu_{0.8}Co_{1.2}O_5$	k_1	$1.35x+1.25z$	1.4K	++Y−−	14
9	$YBaCu_{0.4}Co_{1.6}O_5$	k_2	$2.30x$	1.4 K	+−Y+−	14
10	$YBaCu_{0.5}Fe_{0.5}CoO_5$	k_2	$2.64x$	1.4 K	+−Y+−	17
11	$Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$	$k_2=(0,0,0)$ [b]	$2.2y$	2 K	+−YY+−	4
12	$Y_2SrCuFeO_{6.5}$	$k_2=(0,0,0)$ [b]	$1.36y$	2 K	+−YY+−	4
		$k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ [b]	$1.56x$	2 K	++YY−−	
13	$NdCeBaCu_{0.9}Co_{1.1}O_7$		$0.87z$	5 K	++NdCe−−	present
			$0.56z$	RT	++NdCe−−	
14	$NdCeBaCuFeO_7$		$1.45x$	5 K	++NdCe−−	present

[a] + and − signs here represent the sign of the moment at corresponding layer, Y, Pb or Nd/Ce represent the layers which separate the double Cu/MO_5 layers in the unit cell.

[b] Based on a primitive unit cell related to the body centered cell by $\mathbf{a}_p=-\frac{\mathbf{a}}{2}+\frac{\mathbf{b}}{2}+\frac{\mathbf{c}}{2}$, $\mathbf{b}_p=\frac{\mathbf{a}}{2}-\frac{\mathbf{b}}{2}+\frac{\mathbf{c}}{2}$, and $\mathbf{c}_p=\frac{\mathbf{a}}{2}+\frac{\mathbf{b}}{2}-\frac{\mathbf{c}}{2}$.

B. Magnetic structures of $NdCeBaCuFeO_7$ and $NdCeBaCu_{0.9}Co_{1.1}O_7$

The compound $NdCeBaCuFeO_7$ was first reported by Michel *et al.*[12] Based on powder XRD refinement, the structure of the compound was determined to belong to space group $I4/mmm$ with lattice constants of $a=3.9025$ Å, $c=20.8955$ Å, which agree well with the values obtained in the present study: $a=3.9037(1)$ Å, $c=20.9032(7)$ Å. Although $NdCeBaCu_{0.9}Co_{1.1}O_7$ has not previously been reported, its XRD pattern resembled that of the Fe analog, and its lattice constants were determined to be $a=3.9044(1)$ Å, $c=20.6909(9)$ Å based on the same space group. Rietveld structure refinements, based on neutron data, were therefore carried out for both compounds using the reported $NdCeBaCuFeO_7$ structure as the starting model. The refinement of the room temperature structure of $NaCeBaCuFeO_7$ went smoothly with this model and converged to $R_{wp}=2.77\%$ (Table II). Possible ordering of Cu/Fe and Nd/Ce ions in different sites was tested but no order was detectable. No oxygen vacancies were indicated at any of the three oxygen sites. At 5 K, additional peaks appeared in the Fe-containing samples, which can be indexed as $(\frac{1}{2},\frac{1}{2},1)$ and $(\frac{1}{2},\frac{1}{2},5)$ as shown in Fig. 4(b) and clearly are magnetic in origin. Different trial models of the magnetic moment alignments were investigated and the best fit for the NPD data was obtained for the magnetic structure shown in Fig. 5(a). It must be noted that because the $(\frac{1}{2},\frac{1}{2},0)$ peak is absent, the magnetic moment $[m_x=1.46(3)\mu_B]$ can be uniquely determined as lying in the the x direction with antiparallel spins in the ac plane with B' type centering (or identically in y direction but with A' centering). An essential feature of the model is that the moments of nearby ions within the plane are AFM ordered and those across the plane, through the apical oxygen, order ferromagnetically, which again shows a C type order within the double perovskite slab.

For the $NdCeBaCu_{0.9}Co_{1.1}O_7$ system, additional peaks which violate the extinction rules of the $I4/mmm$ space group appear in both the RT and 5 K NPD patterns, indicating that the AFM magnetic phase transition takes place above room temperature. The main additional peaks can be indexed as $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},1)$. A magnetic model [Fig. 5(b)] similar to that for the Fe analog, but with the moments aligned in the c direction, provided the best fit for both the RT and 5K NPD data [Figs. 4(c),4(d)]. Again FM order through the apical oxygen has been achieved to provide a C type magnetic order. The refinements gave a magnetic moment of $m_z=0.56(5)\mu_B$ at RT and $m_z=0.88(5)\mu_B$ at 5 K for each Cu/Co site.

The ordered magnetic moments found in $NdCeBaCuFeO_7$ and $NdCeBaCu_{0.9}Co_{1.1}O_7$ are significantly lower than those in related layered compounds, e.g., the above Pb containing ones and $PrBaCuFeO_5$,[13] $YBaCuCoO_5$,[14] $Y_2SrCuFeO_{6.5}$, and $Y_2SrCuCoO_{6.5}$.[4] A review of related compounds reveals that nearly all of them (Table III, except those with off stoichiometrc Cu/M ratios) show two kinds of magnetic ordering (C and G type, e.g., appearance of k_1 and k_2) corresponding to the FM and AFM order across the apical oxygen atom. As discussed for the Pb containing samples, these two types of order occur quite separately, with the AFM one apearing at a much lower temperature. The low ordered moments seen in $NdCeBaCuFeO_7$ and $NdCeBaCu_{0.9}Co_{1.1}O_7$ therefore seem to relate the fact that here we observe only FM order and the AFM ordering has not been attained.

With the confirmation of FM $Cud_{z^2}^2 - O2p_z - Fe/Cod_{z^2}^1$ interaction in the present samples, we can regroup all the relevant compounds into Table III. The magnetic structures of the listed compounds are consistent with the GKA rules since inplane $d_{x^2-y^2}^1$-$Op_{x,y}$-$d_{x^2-y^2}^1$ superexchange results in AFM order of the neighboring Cu/M moments in the same layer, whereas across the double layer, $d_{z^2}^2$-$O2p_z$-$d_{z^2}^1$ exchange is FM in nature when the two ions involved are different (one M and one Cu). When the M/Cu ratio is close to 1 and the ions are fully disordered, competition between the FM exchange and the AFM interactions of $d_{z^2}^1$-$O2p_z$-$d_{z^2}^1$ type results in two stages of magnetic phase transitions (compounds 1–5 and possibly 13, 14 in Table III) or in a noncolinear ordering (compound 10). When M/Cu ratio is much greater than 1, the AFM interaction of $d_{z^2}^1$-$O2p_z$-$d_{z^2}^1$ will dominate, and a colinear G type AFM ordering (with only k_2) will appear as in $YBaCu_{0.4}Co_{1.6}O_5$, $YBaCu_{0.5}Fe_{0.5}CoO_5$ and $Y_2SrCu_{.6}Co_{1.4}O_{6.5}$ (compounds 9–11 in Table III).

IV. CONCLUSION

We have found that in mixed Cu/Fe and Cu/Co layered oxides, the magnetic interaction $d_{z^2}^2$-p_z-$d_{z^2}^1$ across the apical oxygen in the Cu-O-Co or Cu-O-Fe linkage is ferromagnetic. However, the inplane AFM $d_{x^2-y^2}^1$-$p_{x,y}$-$d_{x^2-y^2}^1$ superexchange inhibits them from an FM overall structure. It is hoped that with careful choice of magnetic ions in similar structures, one may be able to design new compounds with ferromagnetic interaction in both inplane and out of plane directions. In doing so, one must also bear in mind that the out of plane interaction also includes d_{yz}^2-$O2p_{y,z}$-d_{yz}^1 type which gives the same sign as $Cud_{z^2}^2 - O2p_z - Fe/Cod_{z^2}^1$ in the present compounds but this may not be true for other combinations of TM ions. It is also hoped that this study could shed some light on the magnetic interactions in other TM doped layered cuprates, such as $YBa_2Cu_{3-x}M_xO_7$ (M=Fe, Co) (Refs. 18,19) and more importantly, the so called FM superconductor $RuSr_2GdCu_2O_8$,[20] for all of them share the common Cu-O-TM type linkage.

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