PHYSICAL REVIEW B VOLUME 62, NUMBER 21 1 DECEMBER 2000-I

Magnetic structures of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ and $Y_2SrCuFeO_{6.5}$

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(Received 11 May 2000)

The nuclear and magnetic structures of two layered mixed copper transition-metal oxides $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ and $Y_2SrCuFeO_{6.5}$ have been determined from time-of-flight neutron powder diffraction. Both compounds consist of apex-linked pyramidal Cu/M-O_5 double layers, which alternate with oxygen defective $Y_2O_{1.5}$ fluorite layers. The Co-containing compound has a simple magnetic structure with a Shubnikov group $Ib'a'm$. The magnetic moments $(2.2\mu_B)$ of this compound are aligned along the crystallographic b axis with antiferromagnetic order between neighboring Cu/Co ions. In contrast, the Fe-analog possesses a complicated noncolinear magnetic structure ($Pc'c'n$, with moments $m\perp c$), which can also be considered as comprising two components with $I'bam'$ and $Ib'a'm$ symmetry. The combination of the two components results in an 82° angle between the spins of Cu/Fe ions in neighboring Cu/Fe-O_5 planes within a given double layer. The approximate 90° rotation of the moments results from a ferromagnetic interaction between the neighboring Cu/Fe ions along the c axis through the apical oxygen atoms. The ferromagnetic component may originate from the Cu$d_{z^2}^2$-O2p-Fe$d_{z^2}^1$ type exchange interaction. The implication of such an interaction to related layered cuprates is also discussed. By symmetry analysis, the magnetic structure of the Co compound can be classified as a G_yg type and the appearance of weak ferromagnetism can be attributed to the Dzyaloshinsky-Moria interaction which couples the G_yg mode and F_zf mode in the same representation of the $Ibam$ space group.

I. INTRODUCTION

Magnetic interactions in layered cuprates play a fundamental role in the superconductivity displayed by many of these compounds. Doping the antiferromagnetic (AFM) parent cuprate compounds usually produces a sharp reduction in the AFM transition temperature T_N, and at a sufficiently large hole concentration, superconductivity may occur. Systematic doping studies of layered cuprates, aimed at finding new high-T_c superconductors, have led to the discovery of several interesting layered oxides in which transition-metal (TM) ions occupy some of the copper sites in the Cu-O planes. Although these TM ions often break the superconducting state of the layered cuprates, it may still be of interest to study their effects on the magnetic interactions in the cuprate systems. Of such compounds reported to date, the simplest structure types include $YBaCuFeO_5$,[1] $YBaCuCoO_5$,[2] $Y_2SrCuFeO_{6.5}$,[3] and $(Y,Ce)_nSrCuFeO_y$.[4] The common structural feature of these compounds is the presence of apex-linked double pyramidal MO_5 layers (M=Cu, Fe, Co). The structures are directly related to the superconducting parents $YBa_2Cu_3O_7$ and $(Nd,Ce)_2Ba_2Cu_3O_{9-\delta}$, and are derived by removing the central $BaCuO_2$ chain unit. Similar to most undoped layered cuprates, these compounds are found to show antiferromagnetic order. Recently, Li *et al.* have reported a cobalt substituted layered cuprate,[5] $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$, which, according to x-ray diffraction (XRD), is isostructural with $Y_2SrCuFeO_{6.5}$. Unlike the Fe-containing compound, which shows AFM order below 265K as indicated by magnetization and Mössbauer studies,[3] the Co analog has a ferromagnetic transition with T_c=385 K. Detailed magnetization studies suggested that the compound is most likely a weak ferromagnet.[6] The magnetization measurements on powder samples have not fully resolved the magnetic structure and could not, for example exclude other possibilities such as ferrimagnetism resulting from a nonunique cation distribution on the Cu/Co sites. In addition, although the nuclear structure of the Fe compound was determined by Kim *et al.* from neutron powder-diffraction (NPD) data, they were unable to solve the magnetic structure from their low-temperature data set. In this report, we describe the magnetic structures of both compounds, which have been determined by time of flight NPD.

II. EXPERIMENT

The preparation of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ has been published elsewhere.[5,6] A powder sample of $Y_2SrCuFeO_{6.5}$ was prepared from Y_2O_3, $SrCO_3$, CuO, and Fe_2O_3. The mixture of starting materials was repeatedly sintered at 1100 °C in air for 36 h to obtain a single phase product. The samples were checked for their purity by XRD with a Siemens D5000 diffractometer. Variable temperature time-of-flight (TOF) NPD patterns of the two compounds were collected at POLARIS (ISIS, RAL, Oxford, UK). Field-cooled (FC) and zero-field-cooled (ZFC) dc magnetizations were measured using a Cryogenics S100 superconducting quantum interference device susceptometer with an applied field of 500 Oe. Structure refinements were performed using the NPD data and the GSAS package.[7]

III. RESULTS

A. Magnetic properties

The XRD patterns of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ and $Y_2SrCuFeO_{6.5}$ showed them to be single phase, and all the diffraction peaks could be indexed with the same space group $Ibam$. The magnetic properties of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$

0163-1829/2000/62(21)/14149(8)/$15.00

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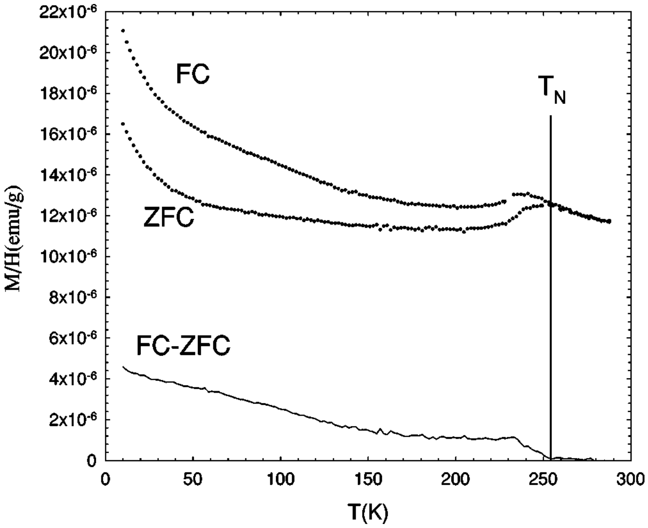


FIG. 1. Field-cooled (top) and zero-field-cooled (middle) magnetic susceptibilities of $Y_2SrCuFeO_{6.5}$, the line at bottom is the difference ($\chi_{FC}-\chi_{ZFC}$) plot.

have been reported elsewhere.[6] A FM moment was observed below $T_c = 385$ K, but the FM moment was only 0.8 emu/g ($0.07\mu_B$ per formula unit) at 4 K. From the temperature dependence of the magnetization, it was speculated that the FM moment originates from spin canting of the AFM ordered moments of the Co and Cu ions. For $Y_2SrCuFeO_{6.5}$, a broad peak around 255 K was observed in the magnetic susceptibility curves for our sample (Fig. 1), which is in general agreement with Ref. 3. In addition, there is a discrepancy between ZFC and FC magnetizations for our sample. Although this feature could possibly indicate the presence of an impurity FM phase (with an ordered moment of 2.3×10^{-3} emu/g at 10 K), the coincidence of T_c with the AFM transition temperature makes this interpretation unlikely. We therefore believe that the signal is intrinsic to the main phase and is indicative of a canted AFM structure, as observed in the Co-containing compound.

B. Structure refinement and nuclear structures

The nuclear structures of the two compounds have previously been reported.[3,6] Rietveld structure refinements in the present study were based on NPD patterns [Figs. 2(a) and

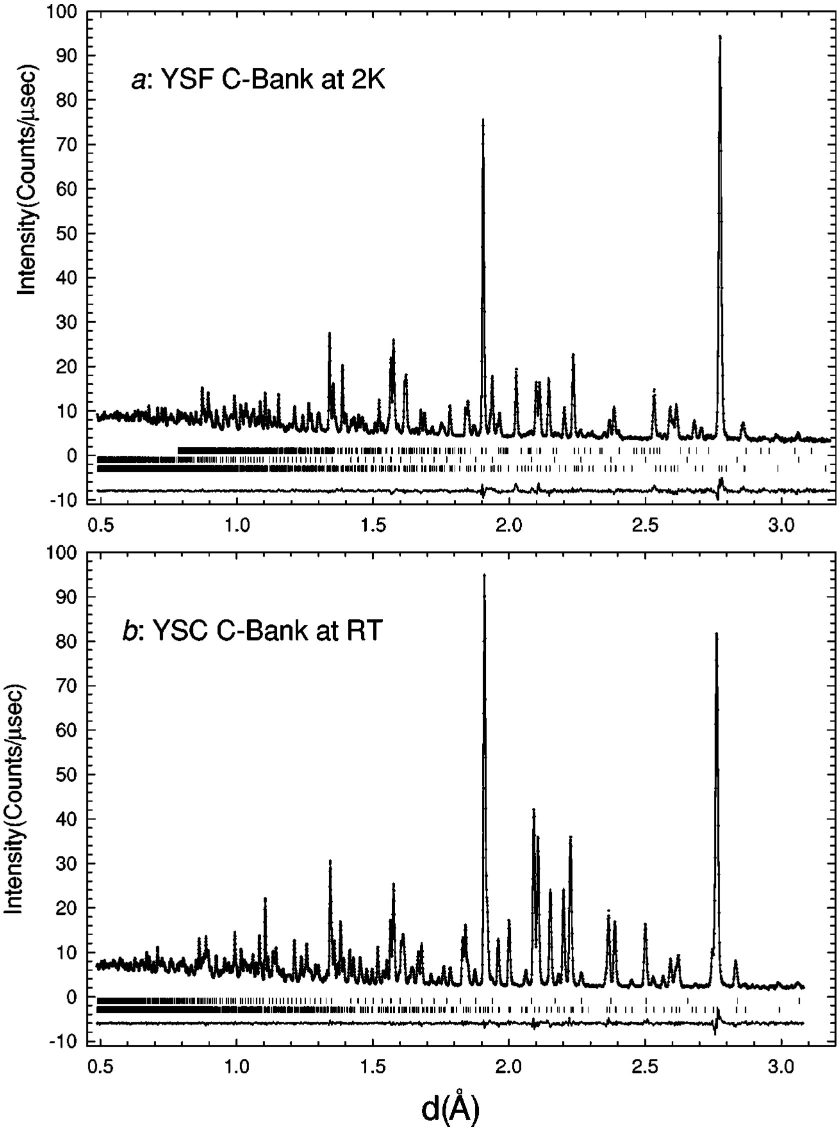


FIG. 2. Neutron-diffraction patterns (C bank) of $Y_2SrCuFeO_{6.5}$ at 2 K (top) and $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ at 290 K (bottom). The dots are observed data, lines are calculated and difference plot, and the vertical marks represent the allowed diffraction peaks (the marks on the middle line in top panel and the upper line in lower panel correspond to Y_2O_3, the marks on top line in the top panel are the positions of magnetic diffraction peaks from the G_xa component, and the marks on the bottom lines of both panels are the peak positions of the diffraction from both nuclear and magnetic G_yg component).

TABLE I. Structural parameters of $Y_2SrCuFeO_{6.5}$ at 2 K (space group $Ibam$, $a=5.408\,13(6)$ Å, $b=10.7111(1)$ Å, $c=20.2412(2)$ Å, $R_{wp}=1.33\%$, $\chi^2=1.940$).

Atoms	x	y	z	U_{iso} (Å ^{2}) [a]
Y	0.2092(1)	0.36192(6)	0.18413(2)	0.0022(1)
Sr	0.2067(2)	0.3657(1)	0	0.0065(2)
Cu/Fe [b]	0.7168(1)	0.38326(5)	0.09807(2)	0.0034(1)
O1	0.1960(2)	0.10894(9)	0	0.0043(2)
O2	0	0.5	0.10631(6)	0.0042(2)
O3	0	0.5	0.25	0.0043(3)
O4	0.5	0.27754(9)	0.25	0.0030(2)
O5	0.4565(2)	0.25276(8)	0.10793(4)	0.0044(1)
O6	0	0	0.35581(5)	0.0039(2)
Bond lengths (Å)	Cu-O1	1.9901(4)	Cu-O2	1.9841(6)
	Cu-O5	1.994(1)	Cu-O5′	1.960(1)
	Cu-O6	1.9520(7)		
Bond angles (°)	Cu-O1-Cu	171.93(7)	Cu-O2-Cu	170.36(7)
	Cu-O5-Cu	167.88(5)	Cu-O6-Cu	122.86(6)

[a] Mean-square atomic displacement, $U_{iso}=B_{iso}/4\pi$.

[b] Ordered moment at this site $m_y=1.36(2)\mu_B$ with magnetic space group $Ib'a'm$ and $m_x=1.56(2)\mu_B$ with $I'bam'$; Cu: Fe $=0.99(2):1.01(2)$.

2(b)] and starting models reported in previous XRD and NPD studies. Both the high-resolution C-bank ($2\theta=145°$, back scattering) and the wide range A-bank ($2\theta=35°$) data were included in the refinements, which employed an interpolated background and pseudo-Voigt profile function. Sample absorption, extinction, and preferred orientation parameters were also refined simultaneously with other structural and instrumental parameters. Since no significant differences were found between the results obtained for the nuclear structure of $Y_2SrCuFeO_{6.5}$ and those determined by Kim *et al.* at room temperature (RT) in the paramagnetic state,[3] only the low-temperature (2 K) data are reported here (Table I). The refined structural parameters of the Co-containing compound at RT and 2 K are listed in Table II.

C. Magnetic structure of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$

For $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ at 2 K and room temperature, peaks which violate the extinction rules of $Ibam$ were apparent and could be indexed with the indices (101) and (103) based on the nuclear unit cell. The peaks were found to disappear above the Curie temperature (385 K, Fig. 3), indicating that they are magnetic in origin. Assuming an AFM interaction between neighboring Co and Cu ions, the magnetic peaks can be satisfactorily modeled only if the moments are

TABLE II. Structural parameters of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ at room temperature [a] and 2 K [b] (second line).

Atoms	x	y	z	U_{iso} (Å ^{2})
Y	0.20646(8)	0.36165(4)	0.18334(2)	0.0043(1)
	0.2058(1)	0.36193(5)	0.18323(2)	0.0008(1)
Sr	0.1965(2)	0.36388(8)	0	0.0093(1)
	0.1959(2)	0.3635(1)	0	0.0032(1)
Cu/Co [a]	0.7111(2)	0.38393(7)	0.09973(4)	0.0081(2)
(at 2 K) [b]	0.7116(2)	0.38397(9)	0.09958(5)	0.0037(1)
O1	0.1887(2)	0.10794(8)	0	0.0101(2)
	0.1874(2)	0.1077(1)	0	0.0035(2)
O2	0	0.5	0.10418(5)	0.0075(2)
	0	0.5	0.10393(7)	0.0035(2)
O3	0	0.5	0.25	0.0053(2)
	0	0.5	0.25	0.0017(3)
O4	0.5	0.27739(7)	0.25	0.0042(2)
	0.5	0.27752(9)	0.25	0.0018(2)
O5	0.4775(1)	0.25218(6)	0.10604(3)	0.0073(1)
	0.4773(1)	0.25199(8)	0.10573(4)	0.0036(1)
O6	0	0	0.35528(4)	0.0077(1)
	0	0	0.35503(6)	0.0042(2)
		Selected bond lengths (Å) and bond angles (°)		
Cu-O1	Cu-O2	Cu-O5	Cu-O5′	Cu-O6
1.9996(7)	2.0051(8)	2.016(1)	1.949(1)	1.9172(9)
1.9924(9)	2.000(1)	2.017(1)	1.942(1)	1.919(1)
	Cu-O1-Cu	Cu-O2-Cu	Cu-O5-Cu	Cu-O6-Cu
RT	171.40(7)	174.92(7)	171.65(5)	124.04(5)
2 K	170.86(9)	175.03(8)	171.79(7)	123.70(7)

[a] Magnetic space group $Ib'a'm$, $a=5.430\,51(6)$ Å, $b=10.7327(1)$ Å, $c=19.9936(2)$ Å, $R_{wp}=1.67\%$, $\chi^2=1.685$, $m_y=1.66(1)\mu_B$; Cu^{2+}: Co^{2+}: $Co^{3+}=0.630(4):0.370(4):1$.

[b] Magnetic space group $Ib'a'm$, $a=5.423\,42(6)$ Å, $b=10.7175(1)$ Å, $c=19.9449(2)$ Å, $R_{wp}=1.19\%$, $\chi^2=1.454$, $m_y=2.18(2)\mu_B$.

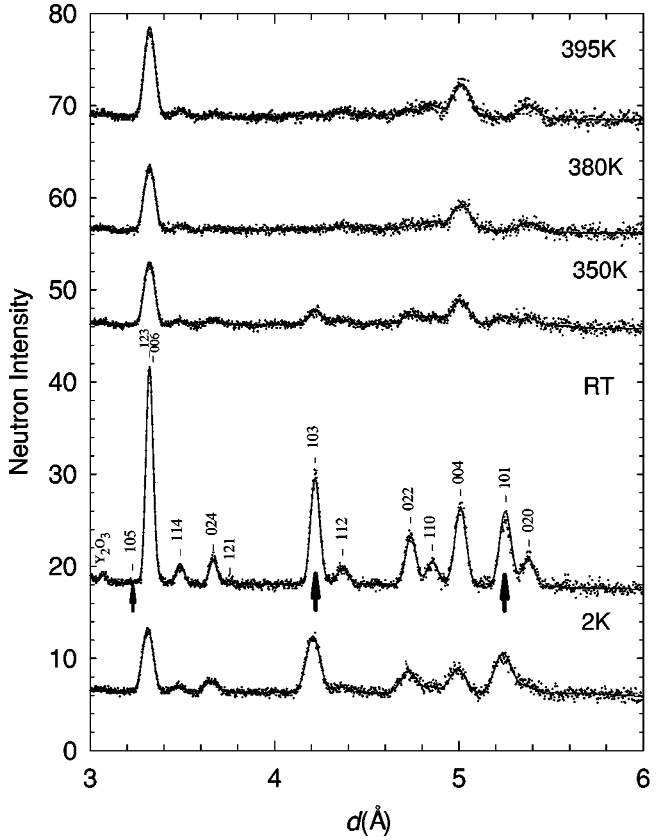
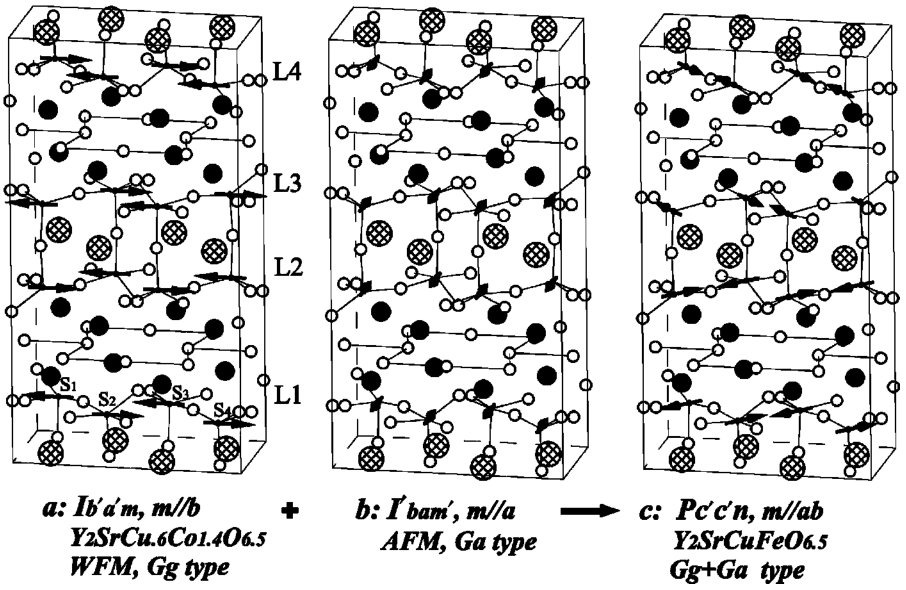


FIG. 3. Neutron-diffraction patterns (*A* bank) of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ at various temperatures, the magnetic diffraction peaks are marked by arrows.

aligned along the crystallographic *b* axis. Thus a final refinement was attempted for a magnetic model with magnetic Schubnikov space group $Ib'a'm$ $[S1=-S2=S3=-S4$ and $L1=-L2=L3=-L4$, Fig. 4(a)]. The refinement quickly converged to good agreement indices with $R_{wp}=1.67\%$, $\chi^2=1.685$ at RT and $R_{wp}=1.19\%$, $\chi^2=1.454$ at 2 K. The ordered magnetic moments at each site were also obtained as $m_y=1.66(1)\mu_B$ at RT and $m_y=2.18(2)\mu_B$ at 2 K. There is no evidence of atomic order at Cu/Co site in the nuclear unit cell. The refinement clearly demonstrates that below T_c the material shows AFM order, and the ferromagnetic (FM) moment must originate from a canting of the spins. Although the space group $Ib'a'm$ does allow a FM component along the *c* direction, attempts to include this component into the refinement resulted in a very small moment ($m_z=0.05\mu_B$/atom at 2 K) with a large estimated standard deviation ($0.03\mu_B$). This moment agrees well with the magnetization measurements,[6] but the value has little quantitative significance in comparison to that derived from the low-temperature magnetization.

D. Magnetic structure of $Y_2SrCuFeO_{6.5}$

The NPD pattern of $Y_2SrCuFeO_{6.5}$ at 2 K has three major additional peaks ($d=5.2$ Å, $d=4.23$ Å, and $d=3.23$ Å when compared to the RT patterns (Fig. 5). Although at first glance it seems that these peaks might also be indexed on the nuclear unit cell with the indices (101), (103), and (105), attempts to account for these peaks on simple magnetic models failed for all simple orientation of the moments; a similar conclusion was reached by Kim *et al.*[3] Close inspection of the diffraction peaks indicated that each is actually composed of two indices: (101)+(021); (103)+(023) and (105)+(025). The former indices in each pair fulfill the condition, $h+k+l=2n$, suggesting that the body centering is preserved in the magnetic space group and a propagation vector of $k_2=(1,1,1)$ can be deduced based on a primitive cell (with basic vectors $\mathbf{a}_p=-\mathbf{a}/2+\mathbf{b}/2+\mathbf{c}/2$, $\mathbf{b}_p=\mathbf{a}/2-\mathbf{b}/2+\mathbf{c}/2$, and $\mathbf{c}_p=\mathbf{a}/2+\mathbf{b}/2-\mathbf{c}/2$).[8] However, the latter indices suggest violation of the body centering condition in the magnetic space group and the propagation vector must be $k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. With these observations in mind, we successfully modeled the peaks with a magnetic structure containing two components: one with $Ib'a'm$ symmetry as for the Co-containing compound, and another with $I'bam'$ symmetry. The magnetic moments of the former component is along the *b* axis [Fig. 4(a)] as for $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ and the moments of the latter component were found to align along the *a* axis [Fig. 4(b)]. It is pertinent to note that in the latter component it is crucial to have a FM arrangement $[L1=-L2=-L3$



a: $Ib'a'm$, m//b + **b: $I'bam'$, m//a** → **c: $Pc'c'n$, m//ab**
$Y_2SrCu_{.6}Co_{1.4}O_{6.5}$ **AFM, Ga type** **$Y_2SrCuFeO_{6.5}$**
WFM, Gg type **Gg+Ga type**

FIG. 4. Crystal and magnetic structure of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ and $Y_2SrCuFeO_{6.5}$. The large shaded circles represent Sr atoms, medium filled circles are Y, small filled circles are Cu/Fe/Co and small open circles are oxygen.

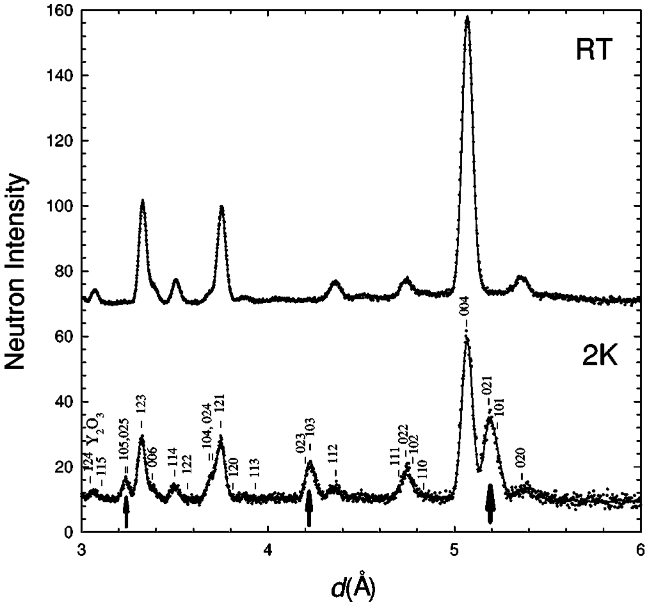


FIG. 5. Neutron-diffraction patterns (A Bank) of $Y_2SrCuFeO_{6.5}$ at room temperature and 2 K, the magnetic diffraction peaks are marked by arrows.

$=L4$, Fig. 4(b)] between the moments on the Cu/Co ions which share the same apex oxygen in the double MO_5 pyramidal layer. The Rietveld refinement based on the above two components gave $R_{wp}=1.33\%$ and $\chi^2=1.940$. The magnetic moment obtained for component $Ib'a'm$ is $m_y=1.36(2)\mu_B$, whereas that for the $I'bam'$ component is $m_x=1.56(2)\mu_B$, with an average moment per site of $|m|=2.07\mu_B$. The magnetic peaks can equally well (with identical agreement indices) be modeled with a magnetic space group $Pc'c'n$, which is the intercept space group between $Ib'a'm$ and $I'bam'$, but with a near perpendicular (82°) arrangement of neighboring Cu/Fe spins across the double MO_5 layer [Fig. 4(c)].

IV. DISCUSSION

The chemical formula $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$, requires that the valence states of the magnetic ions are $0.6Cu^{2+}(d^9)$, $0.4Co^{2+}(d^7)$, and $1Co^{3+}(d^6)$. Assuming that Co^{2+} is in the expected high spin (HS) state as found in related compounds,[9,10] the average ordered moment of $2.18\mu_B$ at 2 K is consistent with Co^{3+} being in an intermediate spin (IS) state. In this case, the average spin only moment for ions at each site can be calculated as $0.3(Cu^{2+},1\mu_B)+0.2[Co^{2+}$ (HS), $3\mu_B]+0.5[Co^{3+}$ (IS), $2\mu_B]=1.9\mu_B$, in reasonable agreement with the refined moment. However, for the Fe-containing compound, the ordered moment is only $2.07\mu_B$, and a HS state must be assigned to the Fe^{3+} ion since IS or low spin (LS) states of Fe^{3+} are very rare among the oxides. In this case the estimated spin only moment will be $3\mu_B$ per site, and the NPD derived value is 30% lower. We therefore sought a different explanation for the moment reduction, one possibility being the two dimensionality of the compound, since it is known that the ordered Cu moment can be reduced to $0.6\mu_B$ (or even $0.4\mu_B$) from its theoretical spin only value ($1\mu_B$) in layered cuprates.[11] If we assume a similar reduction rate for the ordered moments of the Fe and Co substituted materials, and assume that the Co^{3+} is also in the HS state, an ordered moment of $2\mu_B$ can be estimated for $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ based on the spin only moments of the Cu and Co ions, which is in good agreement with the refined value. The small discrepancy can be accounted for by orbital contributions from the Co ions. It can therefore be concluded that both the Co^{2+} and Co^{3+} ions in $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ are in HS states.

In order to better describe the magnetic structures and understand the origin of the appearance of weak ferromagnetism (or canted AFM) in the title compounds, it is helpful to perform a symmetry analysis. There are 16 equivalent magnetic ions in the nuclear cell: the magnetic moments of the four ions within one layer may be represented as $S1$, $S2$, $S3$, and $S4$ and the magnetic moments of ions in successive layers may be represented as $L1$, $L2$, $L3$, and $L4$ [as shown in Fig. 4(a)]. Following Bertaut,[12] we can define

$$F=S1+S2+S3+S4,$$

$$G=S1-S2+S3-S4,$$

$$C=S1+S2-S3-S4,$$

$$A=S1-S2-S3+S4,$$

and similarly

$$f=L1+L2+L3+L4,$$

$$g=L1-L2+L3-L4,$$

$$c=L1+L2-L3-L4,$$

$$a=L1-L2-L3+L4.$$

Applying all symmetry operations of the space group $Ibam$ on the above vectors, we obtained all the representations of $Ibam$ with the above vectors as the basis set (Table III). The table indicates that the magnetic structure of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ actually belongs to the G_yg type, whereas that of the Fe analog belongs to G_yg and G_xa type.

It is now understood that the in-plane Co-O-Co, Co-O-Cu or Cu-O-Cu couplings all give AFM ordering (G type) based on the same $d^1_{x^2-y^2}$-$2p$-$d^1_{x^2-y^2}$ superexchange interaction since in Cu^{2+}, Co^{2+}(HS), and Co^{3+}(HS) the $d_{x^2-y^2}$ orbitals are all half populated. In the c direction, the superexchange interactions across the apical oxygen atom within the double pyramidal layer are complicated. The Co^{2+}-O-Co^{3+}, Co^{2+}-O-Co^{2+}, or Co^{3+}-O-Co^{3+} interactions, all with a $d^1_{z^2}$-O$2p$-$d^1_{z^2}$-type superexchange, will favor an AFM ground state, whereas the exchange pathway $Co^{2+}/Co^{3+}(d^1_{z^2})$-O$2p$-$Cu^{2+}(d^2_{z^2})$ may provide a FM interaction. However, in the Co-containing phase, $Co/Cu \gg 1$, such that the AFM interaction may well dominate and lead to an overall AFM interaction across the double layer ($L1=-L4$, $L2=-L3$). In contrast, the interaction between the double layers is difficult to predict since it involves the M-O-Y-O-M pathways through the defective fluorite $Y_2O_{1.5}$ layer, but the observation of three-dimensional AFM ordering (Gg type) at 385 K in the sample means that it is also an AFM interaction.

TABLE III. Symmetry analysis for the space group $Ibam$.

Symmetry $b\ a\ m\ I$	Representations x	 y	 z	Magnetic space group
$++++$	Gg	Cc	Aa	$Ibam1'$
$-+++$	Ac	Fg	Gf	$Ib'am$
$+-++$	Fg	Ac	Ca	$Iba'm$
$--++$	Cc	Gg	Ff	$Ib'a'm$
$++-+$	Gf	Ca	Ac	$Ibam'$
$-+-+$	Aa	Ff	Gg	$Ib'am'$
$+--+$	Ff	Aa	Cc	$Iba'm'$
$---+$	Ca	Gf	Fg	$Ib'a'm'$
$+++-$	Gc	Cg	Af	$I'bam$
$-++-$	Ag	Fc	Ga	$I'b'am$
$+-+-$	Fc	Ag	Cf	$Iba'm$
$--+-$	Cg	Gc	Fa	$I'b'a'm$
$++--$	Ga	Cf	Ag	$I'bam'$
$-+--$	Af	Fa	Gc	$I'b'am'$
$+---$	Fa	Af	Cg	$I'ba'm'$
$----$	Cf	Ga	Fc	$I'b'a'm'$

From the symmetry analysis, an F_zf-type ordering belongs to the same representation as the G_yg type. The antisymmetric part of the interaction,

$$H_{anti}=A_{ij}S_i\times S_j=D_{yz}(G_yg)(F_zf),$$

known as Dzyaloshinsky-Moria (DM) interaction,[13] will mix them together, and cant the spins towards the z direction. From the refined value of the ordered AFM moments at 2 K, and the measured FM moment at low temperature[6] we can work out that the canting angle of the spins from b towards c in $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ is: $\theta=\tan^{-1}(0.035/2.18)=0.92°$. A similar calculation for the small FM moment in the Fe analog gives a canting angle of 0.003°.

Though the magnetic structure of $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ is clarified, our understanding of the magnetic order in $Y_2SrCuFeO_{6.5}$ is incomplete. The NPD refinement indicates that it is composed of two components, $Ib'a'm(G_yg)$ and $I'bam'(G_xa)$, which may mean that on cooling from the paramagnetic phase, the compound undergoes two different phase transitions and orders into two magnetic phases (or separate domains). However, there is no indication of two types of magnetic ordering in the magnetization measurements (Fig. 1 and Ref. 3) rather a single transition temperature was observed, which contradicts the above interpretation. Alternatively, the two components may join together to give a noncolinear magnetic structure as shown in Fig. 4(c). In this case, the magnetic moments are aligned with the in-plane Fe/Cu-O bonds, and although those across the double layer are nearly perpendicular to each other, the spins within each plane are still antiparallel. It is known that the in-plane exchange interaction through the Fe-O-Cu, Fe-O-Fe, or Cu-O-Cu, all give the AFM ordering (similar to the situation in the Co analog) because their $d_{x^2-y^2}$ orbitals are also all half occupied. Thus a G-type ordering can be expected via the $d^1_{x^2-y^2}$-$p_{x,y}$-$d^1_{x^2-y^2}$ superexchange interaction. In the z direction, while the interaction through the double fluorite $Y_2O_{1.5}$ layer is AFM as in the Co phase, of the interactions across the double pyramidal layer, Cu-O-Fe may give FM interaction via Cu$d^2_{z^2}$-O2p_z-Fe$d^1_{z^2}$ exchange, but Fe$d^1_{z^2}$-O2p_z-Fe$d^1_{z^2}$ superexchange will favor AFM ordering (the exchange through Cu-O-Cu in z direction can be neglected for there is no direct overlapping between the Cu$d^1_{x^2-y^2}$ and oxygen orbitals involved). If the Cu/Fe ions are ordered into separate layers, a pure FM ordering through the double layer will be observed. However, both the nuclear structure determination and the magnetic structure provide no evidence to support such order in $Y_2SrCuFeO_{6.5}$. It is therefore possible that the AFM and FM interactions across the double pyramidal layer are of similar strength and result in a noncolinear AFM structure with 82° between moments on neighboring Cu/Fe ions.

At this stage, we may compare the magnetic structures of $Y_2SrCuFeO_{6.5}$ and $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ with those reported for related compounds (listed in Table IV). Note that except for the compounds studied here, all possess tetragonal symmetry ($P4/mmm$), where an ambiguity of the spin alignment in the x,y direction necessarily occurs. For $YSrCuFeO_5$,[14] $RBaCuFeO_5$,[15,17] and $YBaCuCoO_5$,[16] the appearance of $k_2=(\frac{1}{2},\frac{1}{2},1)$ definitely indicates that the interaction across the double layer is AFM, while observation of $k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ may mean it is AFM or FM or a mixture of both. The latter ambiguity is due to the fact that the structure of these compounds is closely related to the perovskite structure, and with $z_{Cu/Fe}\approx0.25$ it is impossible to differentiate between the spin arrangements $++Y--$ (a type) and $+-Y-+$ (c type, Table IV). In the $YBaCo_{2-x}Cu_xO_5$ and $YBaCoFe_{1-x}Cu_xO_5$ systems,[9,10] when $1\geqslant x\geqslant0.8$ only k_1 was observed and when $x=0.4$ and 0.5 only k_2 was observed. The latter case is identical to our Co phase ($x=0.6$) where AFM order across the double MO_5 layer was also observed. In the former case, together with those for $YSrCuFeO_5$ and $RBaCuFeO_5$, k_1 was always observed (k_2 was also observed for $YSrCuFeO_5$ and $RBaCuFeO_5$). These observations are all consistent with the assumption that in-plane $d^1_{x^2-y^2}$-$p_{x,y}$-$d^1_{x^2-y^2}$ superexchange results in AFM G-type order of the Cu/M moments in the same layer, whereas across the double layer $d^2_{z^2}$-O2p_z-$d^1_{z^2}$ exchange is FM in nature when the two ions involved are different (one M and one Cu). Ordering of Cu and M ions into separate layers would provide a solely FM interaction and such order has been proposed for $YBaCuFeO_5$ based on NPD.[18] 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 $d^1_{z^2}$-O2p_z-$d^1_{z^2}$ type results in a noncolinear ordering (compounds 1, 2, 10, and possibly 3, 4, 5, 6 in Table IV). When M/Cu ratio is much greater than 1, the AFM interaction of $d^1_{z^2}$-O2p_z-$d^1_{z^2}$ will dominate, and a colinear Gg-type (with only k_2) ordering will appear as in $YBaCu_{0.4}Co_{1.6}O_5$, $YBaCu_{0.5}Fe_{0.5}CoO_5$, and $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$.

If we make the additional assumption that the interaction across the Y layers is always AFM (which is supported by the magnetic structures of compounds 7, 8, 9, and 10), we can understand all the magnetic structures in Table IV based on the above superexchange AFM interactions of $d^1_{x^2-y^2}$-O$p_{x,y}$-$d^1_{x^2-y^2}$ and $d^1_{z^2}$-Op_z-$d^1_{z^2}$ and their competition

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

Case	Compounds	Prop. vector	Moment (μ_B)	Temperature	Spin direction [a]	Mode	Reference
1	$YSrCuFeO_5$	$k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$1.5z+0.2x$	2 K	$++Y--$ or $+-Y-+$	*a* or *c*	14
		$k_2=(\frac{1}{2},\frac{1}{2},1)$	$1.6y$	2 K	$+-Y+-$	*g*	
2	$PrBaCuFeO_5$	k_1	$1.18z+0.7x$	2 K	$++Y--$ or $+-Y-+$	*a* or *c*	15
		k_2	$1.53x$	2 K	$+-Y+-$	*g*	
3	$YBaCuFeO_5$	k_1	$1.32x+0.74z$	RT	$++Y--$ or $+-Y-+$	*a* or *c*	17
		k_2	?	<200 K	$+-Y+-$	*g*	17
4	$YBaCuFeO_5$	k_1	$0.65x+1.46z$	RT	$++Y--$ or $+-Y-+$	*a* or *c*	18
5	$YBaCuCoO_5$	k_1	$1.48z$	RT	$++Y--$	*a*	16 [b]
6	$YBaCu_{0.8}Co_{1.2}O_5$	k_1	$1.35x+1.25z$	1.4 K	$+-Y-+$	*c*	9 [b]
7	$YBaCu_{0.4}Co_{1.6}O_5$	k_2	$2.30x$	1.4 K	$+-Y+-$	*g*	9
8	$YBaCu_{0.5}Fe_{0.5}CoO_5$	k_2	$2.64x$	1.4 K	$+-Y+-$	*g*	10
9	$Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$	$k_2=(1,1,1)$ [c]	$2.2y$	2 K	$+-YY+-$	*g*	present
10	$Y_2SrCuFeO_{6.5}$	$k_2=(1,1,1)$ [c]	$1.36y$	2 K	$+-YY+-$	*g*	present
		$k_1=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ [c]	$1.56x$	2 K	$++YY--$	*a*	

[a] + and − signs here represent the sign of the moment at corresponding layer (i.e., $+L_i, -L_i$), Y represents the ytrium layers in the unit cell.

[b] Due to $z_{Cu/Co}\approx 0.25$, the spin directions arrangement along *c* axis cannot be determined uniquely, both *a* and *c* type should be considered although not given in the literature.

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

with the FM exchange $d_{z^2}^2$-O2p_z-$d_{z^2}^1$. In this case, if only k_1 is observed (as in $YBaCuFeO_5$, $YBaCuCoO_5$, and $YBaCu_{0.8}Co_{1.2}O_5$), the interaction between the double layer is FM, which can only occur if some degree of Cu, Fe, Co ordering takes place, such as reported in Ref. 18. If only k_2 is observed, as in the case of $YBaCu_{0.4}Co_{1.6}O_5$, $YBaCu_{0.5}Fe_{0.5}CoO_5$, and $Y_2SrCuCoO_{6.5}$, the interaction across the double layer is AFM, which suggests that the Co-O-Co or Co-O-Fe AFM interactions exceed the FM Cu-O-Co or Cu-O-Fe interactions. If both k_1 and k_2 are observed, as in $YSrCuFeO_5$, $PrBaCuFeO_5$, and $Y_2SrCuFeO_{6.5}$ and implying a noncolinear magnetic structure, then the Cu-O-Fe FM interaction is comparable with the AFM Fe-O-Fe superexchange. This mixed AFM and FM interactions may require the Cu/Fe ions being completely disordered which is indeed observed in these three samples.

In conclusion, the nuclear and magnetic structures of the title compounds were solved from TOF NPD data. $Y_2SrCu_{0.6}Co_{1.4}O_{6.5}$ has a G_yg-type ordered magnetic structure with space group $Ib'a'm$ while $Y_2SrCuFeO_{6.5}$ has a complicated noncolinear structure which can be resolved into two components, one of G_yg type and the other of G_xa type. Such ordering is directly related to their valence states and composition. With all the TM elements in their HS states, it can be predicted that within the Cu/M-O_5 plane, order should be of the AFM G type in both compounds. An off-stoichiometric M/Cu ratio will result in an AFM order across the double layer, whereas a 1:1 M/Cu ratio will result in a FM component through $d_{z^2}^2$-O2p_z-$d_{z^2}^1$-type interaction. The observation of small FM magnetic moments in the samples was explained with the DM canting mechanism.

ACKNOWLEDGMENTS

We are grateful to EPSRC for funding this work and providing neutron-diffraction facilities. The authors would like to thank Dr. R. I. Smith for his assistance in collecting the NPD data.

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