Room-temperature ferromagnetism in $Sr_{1-x}Y_xCoO_{3-\delta}$ ($0.2 \leq x \leq 0.25$)

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We have measured magnetic susceptibility and resistivity of $Sr_{1-x}Y_xCoO_{3-\delta}$ ($x=0.1$, 0.15, 0.2, 0.215, 0.225, 0.25, 0.3, and 0.4), and found that $Sr_{1-x}Y_xCoO_{3-\delta}$ is a room temperature ferromagnet with a Curie temperature of 335 K in a narrow compositional range of $0.2 \leq x \leq 0.25$. This is the highest transition temperature among perovskite Co oxides. The saturation magnetization for $x=0.225$ is 0.25 μ_B/Co at 10 K, which implies that the observed ferromagnetism is a bulk effect. We attribute this ferromagnetism to a peculiar Sr/Y ordering.

I. INTRODUCTION

Transition-metal oxides with perovskite-based structure exhibit many fascinating phenomena such as colossal magnetoresistance in Mn oxides,[1] high temperature superconductivity in Cu oxides,[2] and ferroelectricity in Ti oxides.[3] Perovskite Co oxides also show very rich physics such as spin-state transition,[4,5] ferromagnetism,[6] and thermoelectricity.[7] The ferromagnetism in the perovskite Co oxide $La_{1-x}Sr_xCoO_3$ has been explained in terms of the double–exchange interaction between Co^{3+} and Co^{4+} in the intermediate spin state. The ferromagnetic transition temperature (T_c) is 270 K at highest, which is significantly lower than T_c=370 K of perovskite Mn oxides at an optimum composition.

In recent years, the A-site ordered perovskite $RBaCo_2O_{5.5}$ (R=rare earth element) has been intensively studied.[8–10] It shows a ferromagnetic transition around 300 K (higher than T_c of $La_{1-x}Sr_xCoO_3$) with giant magnetoresistance.[8,11] In addition, a transition from the ferromagnetic state to an antiferromagnetic state is seen around 255 K in the magnetization.[10] The complicated magnetism has been explained as follows: The Co^{3+} ions in the intermediate spin (IS) state of $S=1$ exhibit an orbital ordering at 350 K along the a axis,[9] which induces ferromagnetic interaction along the a axis. On the other hand, antiferromagnetic interaction is expected along the b axis because of the conventional superexchange, which causes the antiferromagnetic order below 270 K. At higher temperatures, thermally excited carriers induce the double-exchange interaction to align the ferromagnetic chains, and stabilizes the ferromagnetic state from 270 to 300 K.[8,9]

Very recently, Withers *et al.*[12,13] and Istomin *et al.*[14,15] independently reported a new A-site ordered perovskite Co oxide $Sr_{1-x}R_xCoO_{3-\delta}$ (R=Y and lanthanide). According to

their structure analysis, Sr and R are ordered because of the different ionic radii. The R ions prefer to occupy at every two sites in the ab plane, which doubles the lattice parameter of the a and b axes from the primitive perovskite cell. The ordered ab planes are stacked along the c axis in units of four cells, and the c axis length quadruples that of the primitive cell. This will give an ideal composition of $Sr_{0.75}R_{0.25}CoO_{3-\delta}$, but a particular composition near $x=1/3$ has been extensively studied so far. Aside from the cation ordering, the two groups proposed different oxygen ordering structures, and the complete structure is still controversial.

Magnetic properties of $Sr_{1-x}Y_xCoO_{3-\delta}$ were measured only for $x=0.1$ and 0.33,[16,17] and we expected that the peculiar Sr/Y ordering near $x=1/4$ could show a magnetism. We have found that polycrystalline samples of $Sr_{1-x}Y_xCoO_{3-\delta}$ show a ferromagnetic transition at 335 K in a narrow range of $0.2 \leq x \leq 0.25$, which is the highest transition temperature among perovskite Co oxides. The magnetization of the x =0.225 sample is 0.25 μ_B/Co at 10 K, indicating a bulk ferromagnet. We suggest that this ferromagnetism is driven by the orbital ordering, just like the ferromagnetism in $RBaCo_2O_{5.5}$. However, T_c of the former is even higher than that of the latter, and ferromagnetic order survives down to 5 K. We will discuss a possible origin for the difference.

II. EXPERIMENT

Polycrystalline samples of $Sr_{1-x}Y_xCoO_{3-\delta}$ ($x=0.1$, 0.15, 0.2, 0.215, 0.225, 0.25, 0.3, and 0.4) and $Sr_{0.775}R_{0.225}CoO_{3-\delta}$ (R=Dy, Ho, and Er) were prepared by a solid-state reaction. Stoichiometric amounts of $SrCO_3$, Y_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, and Co_3O_4 were mixed, and the mixture was calcined at 1100 °C for 12 h in air. The product was finely ground, pressed into a pellet, and sintered at 1100 °C for 48 h in air,

followed by slow cooling down to room temperature in the furnace. The resultant oxygen content of the sample represented an equilibrium value (in air) was confirmed by means of thermogravimetric annealing experiments. The oxygen content was determined through iodometric titration.[18] A powdered sample of 20–40 mg was dissolved in 1 M HCl solution (∼30 ml) containing an excess of KI. The titration of the formed I_2 was performed against a standard 0.015 M sodium thiosulphate solution using starch as an indicator. For each sample, the analysis was repeated three times in minimum with a reproducibility better than ±0.003 for δ. Throughout this paper, we will use the nominal composition x, although the third decimal point of x includes some uncertainty. We evaluated through energy dispersive x-ray analysis (EDX) the real compositions for $x=0.215$ and 0.225 to be Sr:Y=0.781:0.219 and 0.766 : 0.234, respectively, meaning that x is correct within an accuracy of ±0.01. As a reference, $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$ powder was sealed with $KClO_4$ in a gold capsule, and then treated at 3 GPa and 700 °C for 30 min in a conventional cubic anvil-type high pressure apparatus.

The x-ray diffraction (XRD) of the sample was measured using a standard diffractometer with Fe $K\alpha$ radiation as an x-ray source in the θ-2θ scan mode. The resistivity was measured by a four-probe method, below room temperature (4.2–300 K) in a liquid He cryostat, and above room temperature (300–400 K) in an electronic furnace. The magnetization M was measured from 5 to 400 K by a commercial superconducting quantum interference device (SQUID, Quantum Design MPMS). We applied 0.01–0.1 T for the measurement of $M(T)$ data, and −7–7 T for $M(H)$ data.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the magnetization of $Sr_{1-x}Y_xCoO_{3-\delta}$ at 0.1 T as a function of temperature. A tiny trace of a ferromagnetic transition is seen at 300 K for $x=0.1$ and 0.15, and a weak and broad peak is seen near 300 K for $x=0.3$ and 0.4, which is consistent with the literature.[12,19] Surprisingly, the samples only in a narrow compositional range of $0.2 \leqslant x \leqslant 0.25$ show large magnetization. The ferromagnetic transition temperature (T_c) is 335 K, which is a high temperature in perovskite Co oxides.

The range of $0.2 \leqslant x \leqslant 0.25$ is quite singular, below which or above which the magnetization rapidly fades away. This makes a remarkable contrast with $La_{1-x}Sr_xCoO_3$, where T_c and magnetization continuously change with the Sr content. Thus, the observed ferromagnetism should not be attributed to the double-exchange mechanism.

The inset of Fig. 1(a) shows $M(T)$ of $Sr_{0.775}Y_{0.225}CoO_3$ annealed in high-pressure oxygen. We expect no oxygen vacancies ($\delta=0$) for this sample. Thus the formal valence of Co is more than 3.7, and the magnetism seems to be dominated by the double exchange interaction between Co^{4+} and Co^{3+}. In fact, the observed ferromagnetic state is quite different from that in the oxygen-deficient samples: T_c is remarkably lower, but the magnetization is larger. These features are essentially similar to $M(T)$ of $La_{1-x}Sr_xCoO_3$.[6] These differences clearly reveal that oxygen deficiency is essential to the peculiar room-temperature ferromagnetism.
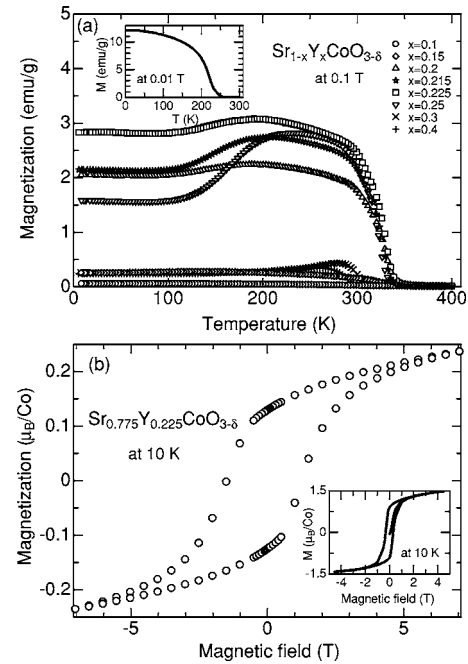

FIG. 1. (a) Magnetization vs temperature $[M(T)]$ of $Sr_{1-x}Y_xCoO_{3-\delta}$ ($x=0.1$, 0.15, 0.2, 0.215, 0.225, 0.25, 0.3, and 0.4); (b) magnetization vs magnetic field $[M(H)]$ of $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$. The insets of (a) and (b) show $M(T)$ and $M(H)$ of $Sr_{0.775}Y_{0.225}CoO_3$, respectively.

Figure 1(b) shows the magnetic-field dependence of the magnetization $[M(H)]$ of $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$ at 10 K. At 7 T, the magnetization reaches 0.25 μ_B/Co. Although this value is somewhat smaller than that of $La_{1-x}Sr_xCoO_3$ (typically more than 1 μ_B/Co), it is large enough to be taken as an indication of bulk ferromagnetism, and is almost equal to that of polycrystalline sample of $GdBaCo_2O_{5.5}$ at 250 K.[11,19] The inset of Fig. 1(b) shows $M(H)$ of $Sr_{0.775}Y_{0.225}CoO_3$ (the annealed sample) at 10 K in which the $M(H)$ curve is quantitatively different from that in the nonannealed samples. These experimental facts further consolidate that the ferromagnetism in $Sr_{1-x}Y_xCoO_{3-\delta}$ is not caused by the double-exchange mechanism.

Figure 2(a) shows the XRD pattern of $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$, which is consistent with those of Refs. 12–15. All the peaks are indexed as a tetragonal cell of the space group $I4/mmm$ with the lattice parameters of $a=7.674$ Å and $c=15.34$ Å, except for small peaks of Y_2O_3 (at most 2%; note that the intensity scale is logarithmic). Note that the $(h00)$, $(0k0)$, $(00l)$ ($h,k,l \neq 2n$) peaks do not appear according to the extinction rule.

Figure 2(b) shows the XRD pattern of $Sr_{0.775}Er_{0.225}CoO_{3-\delta}$, where all the peaks except for small peaks of Er_2O_3 (at most 4%) are again successfully indexed as the tetragonal cell. The only difference from Fig. 2(a) is that the (101), (110), and (103) peaks are much stronger in Fig. 2(b). This should be associated with the different x-ray scattering cross sections of Er and Y, directly indicating that these superstructure peaks come from the A-site ordering. In other words, if the A site cations were disordered (but the Co or O ions were ordered), the two XRD patterns should be
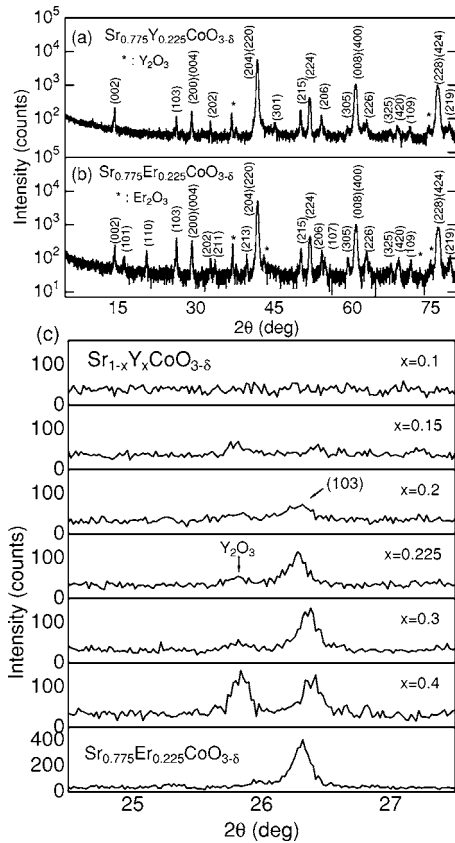
FIG. 2. X-ray diffraction patterns of (a) $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$ and (b) $Sr_{0.775}Er_{0.225}CoO_{3-\delta}$; (c) x-ray diffraction patterns around 26° of $Sr_{1-x}Y_xCoO_{3-\delta}$ (x=0.1, 0.15, 0.2, 0.225, 0.3, and 0.4) and $Sr_{0.775}Er_{0.225}CoO_{3-\delta}$.

FIG. 3. Magnetization vs temperature of $Sr_{0.775}R_{0.225}CoO_{3-\delta}$ (R=Y,Dy, Ho, and Er). The inset shows $1/M$ of $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$.

identical. Although the possibility of the ordering of the Co and O ions is not excluded, the above results strongly support that the A-site ordering is predominant.[20]

Figure 2(c) shows the x dependence of the (103) peak, which is a direct probe for the A-site ordering. Clearly, it appears above x=0.2, which exactly corresponds to the emergence of the room-temperature ferromagnetism in this compound. As listed in Table I, the crystal symmetry for x=0.1 and 0.15 is cubic ($Pm3m$) without any superstructure peaks like the (103) peak in Fig. 2(a), which is consistent with Ref. 15. Thus we conclude that the A-site ordering drives the ferromagnetism in the Co ions. This is the same
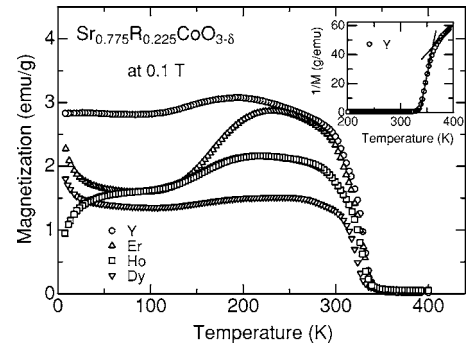
situation as in the case of $RBaCo_2O_{5.5}$, where the ordering of R and Ba stabilizes the Co^{3+} ordering. Thus we think that the ferromagnetism in the present material would be driven by the orbital ordering, although the ordering pattern may be different because $RBaCo_2O_{5.5}$ shows a different XRD pattern. We further note that the peak is monotonically shifted to a higher degree with increasing x, indicating that the lattice parameter is systematically decreased by substitution of Y for Sr (see Table I). On first glance, it looks inconsistent that the x=0.3 sample does not show the bulk ferromagnetism in spite of having the same intensity of the (103) peak as the x=0.25 sample. We think that the ferromagnetism is quite susceptible to the Sr/Y solid solution in the Sr site: Y cannot help occupying the Sr site for $x>1/4$. In fact, our conjecture is verified by the fact that $Sr_{0.75-y}Ca_yY_{0.25}CoO_{3-\delta}$ rapidly loses ferromagnetism with y.[21] In contrast, the oxygen content is unlikely to play an important role, because it remains essentially constant ($3-\delta$=2.64) between x=0.25 and 0.3.

Figure 3 shows the $M(T)$ of $Sr_{0.775}R_{0.225}CoO_{3-\delta}$ (R=Y,Dy, Ho, and Er). Not only the Y-substituted samples but also the other compounds exhibit a similar ferromagnetism below 335 K. This means that the magnetic moments of the lanthanides are irrelevant to the 335 K transition. The inset of Fig. 3 shows $1/M$ of $Sr_{0.775}Y_{0.225}CoO_{3-\delta}$, in which a kink is observed at 360 K. A similar kink was observed in $1/M$ of $TbBaCo_2O_{5.5}$ at the orbital-ordering temperature.[9]

The low-temperature magnetization is affected by the magnetic moment of Dy^{3+}, Ho^{3+}, and Er^{3+}. The low-temperature susceptibility of the Er- and Dy-substituted

TABLE I. Crystallographic and iodometric titration data for $Sr_{1-x}Y_xCoO_{3-\delta}$ (x=0.1, 0.15, 0.2, 0.225, 0.25, 0.3, and 0.4). Standard deviation is given in parentheses.

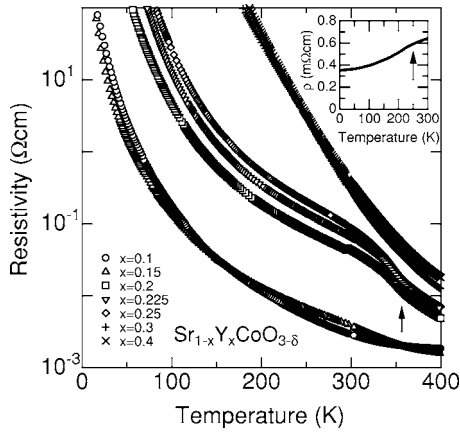| x	a (Å)	c (Å)	Space group	$3-\delta$	Co valence
0.1	3.853(1)	—	$Pm3m$	2.695(3)	3.289
0.15	3.847(1)	—	$Pm3m$	2.690(1)	3.230
0.2	7.685(7)	15.37(1)	$I4/mmm$	2.655(0)	3.110
0.225	7.674(8)	15.34(1)	$I4/mmm$	2.650(3)	3.075
0.25	7.664(8)	15.32(1)	$I4/mmm$	2.641(0)	3.033
0.3	7.647(7)	15.26(1)	$I4/mmm$	2.643(2)	2.985
0.4	7.649(7)	15.24(1)	$I4/mmm$	2.634(2)	2.865

FIG. 4. Resistivity of $Sr_{1-x}Y_xCoO_{3-\delta}$ (x=0.1, 0.15, 0.2, 0.225, 0.25, 0.3, and 0.4). The arrow indicates the kink temperature in the inset of Fig. 3. The inset shows the resistivity of $Sr_{0.775}Y_{0.225}CoO_3$. The arrow indicates the Curie temperature.

samples obeys the Curie law below about 50 K. The effective magnetic moment is evaluated to be 6.7 μ_B/Er for the Er-substituted sample, corresponding to 70% of that expected from Er^{3+} of J=15/2 and g=6/5, where J is the total angular momentum and g is Lande's g factor. The effective magnetic moment is 5.3 μ_B/Dy for the Dy-substituted sample, corresponding to 50% of that expected from Dy^{3+} (J=15/2 and g=4/3). Since the orbital angular momentum is sometimes quenched in the presence of ligand field, the magnetic moments are reasonably evaluated for the above samples. On the other hand, the Ho-substituted sample shows anomalous susceptibility that decreases with decreasing temperature below 50 K. It may indicate an antiferromagnetic coupling between Co^{3+} and Ho^{3+} ions, and such a $3d-4f$ coupling is actually observed in $R_2Cu_2O_5$.[22]

Figure 4 shows the resistivity of $Sr_{1-x}Y_xCoO_{3-\delta}$. The temperature dependence of resistivity is nonmetallic, which is again incompatible with the double-exchange mechanism. For $0.2 \le x \le 0.25$ samples, a resistivity jump is seen at 360 K, which is close to T_c. A similar but larger jump was reported in the resistivity of $GdBaCo_2O_{5.5}$.[8,19,23] We further note that the resistivity for $0.2 \le x \le 0.25$ is clearly distinguished from that for $x \le 0.15$ or $x \ge 0.3$. The inset of Fig. 4 shows the resistivity of $Sr_{0.775}Y_{0.225}CoO_3$ annealed in the high-pressure oxygen. The resistivity shows metallic conduction with a kink at 250 K, which is very different from the resistivity of the nonannealed samples.

Now we discuss the origin of the room-temperature ferromagnetism in $Sr_{1-x}Y_xCoO_{3-\delta}$ ($0.2 \le x \le 0.25$). As listed in Table I, the oxygen content 3-δ for x=0.25 is ~2.64, corresponding to the formal Co valence of ~3.03. This is in between the oxygen content of 2.69 for x=0.2 by James *et al.*[13] and the oxygen content of 2.62 for x=0.3 by Istomin *et al.*[14] Very recently, Maignan *et al.*[17] found a similar oxygen content of 2.66 for x=0.33, and reported that the formal valence

of Co is 2.99. From these data we believe that the Co ions are essentially trivalent for x=0.25. Thus, the ferromagnetism most likely arises from the orbital ordering of the IS Co^{3+} ions, as in the case of $RBaCo_2O_{5.5}$, which naturally explains the several similarities to the ferromagnetism in $RBaCo_2O_{5.5}$ mentioned above.

Next, we will compare $Sr_{1-x}Y_xCoO_{3-\delta}$ with $RBaCo_2O_{5.5}$. The ferromagnetic order is highly robust down to 5 K in $Sr_{1-x}Y_xCoO_{3-\delta}$, and is most likely the ground state of this system. According to the theory of orbital ordering,[24] an antiferrotype orbital order favors a ferromagnetic order, and a ferrotype orbital order favors an antiferromagnetic order. Suppose the present compound be an insulator consisting of IS Co^{3+}. Then an orbital order will be antiferrotype, and prevent formation of the e_g band, which drives a ferromagnetic order. Similar ferromagnetic states are seen in other orbital-ordered systems, such as K_2CuF_4[24] and $YTiO_3$.[25] In this context $RBaCo_2O_{5.5}$ is rather exceptional, in which the antiferromagnetic order is the ground state in spite of the antiferrotype orbital ordering. Thus the ferromagnetic state competes with the antiferromagnetic state in $RBaCo_2O_{5.5}$, which causes large magnetoresistance. Such a competition can explain why T_c is lower than T_c of $Sr_{1-x}Y_xCoO_{3-\delta}$.

Finally, we would like to add a few notes: (i) As a preliminary measurement, we measured the magnetoresistance of $Sr_{0.775}Y_{0.225}CoO_{2.65}$ at 300 K. The value is −0.5% at 7 T, which is very small compared with that of a typical giant magnetoresistance material. This suggests that the ground state is ferromagnetic and insulating, which is consistent with our orbital-ordering scenario. (ii) We examined an impurity effect, and observed that the ferromagnetism is quite susceptible against impurities, where only a 1% substitution of Mn for Co destroys a half of the saturation magnetization. Such result cannot be understood from simple dilution effects, and could be attributed to the impurity effect on the orbital ordering. In a case of charge ordering, a tiny disorder strongly suppresses the charge ordering state.[26]

IV. SUMMARY

We have measured magnetic susceptiblity and resistivity of $Sr_{1-x}Y_xCoO_{3-\delta}$ (x=0, 0.1, 0.15, 0.2, 0.225, 0.25, 0.3, and 0.4), and have found that $Sr_{1-x}Y_xCoO_{3-\delta}$ for $0.2 \le x \le 0.25$ can be regarded as a room-temperature ferromagnet. The ferromagnetic transition temperature is ~335 K, which is the highest transition temperature among perovskite Co oxides. The magnetization of the x=0.225 sample at 10 K is 0.25 μ_B/Co, which implies a bulk ferromagnet. We conclude that the ferromagnetic order is driven by the peculiar Y/Sr ordering. We expect that this material will open a new window to materials science of the A-site ordered Co oxides.

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