Valence and spin state of Co and Ni ions and their relation to metallicity and ferromagnetism in $LaCo_{0.5}Ni_{0.5}O_3$

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$LaNi_{0.5}Co_{0.5}O_3$ was measured in terms of x-ray-absorption near-edge structure (XANES), powder x-ray diffraction, magnetic susceptibility, resistivity, and heat capacity. A small but clear heat capacity anomaly and an ac susceptibility peak were observed at 53 K. The peak temperature and magnitude of the ac susceptibility were found to be, respectively, independent of and dependent on frequency. The magnetization reversal at the coercive force is sharp but the magnetization does not saturate even at 50 kOe and 5 K. The resistivity is on the order of 10^{-3} Ω cm and the contribution from conductive electrons to the heat capacity was observed at low temperatures. These results are consistent with the earlier conclusion that $LaCo_{0.5}Ni_{0.5}O_3$ is a metallic ferromagnet with a certain disorder with respect to magnetic interaction. XANES indicated that both valences of Co and Ni ions are trivalent. The unit-cell volume is larger than that of either $LaCoO_3$ or $LaNiO_3$ below room temperature, which suggests that the population of Co e_g orbitals of $LaCo_{0.5}Ni_{0.5}O_3$ is larger than that of $LaCoO_3$. The presence of itinerant σ^* electrons and t_{2g} holes was proposed as necessary conditions to show the ferromagnetism not only in $LaCo_{1-x}Ni_xO_3$ but also in $SrFe_{1-x}Co_xO_3$, $SrCoO_3$, and $Sr_{1-x}La_xCoO_3$.

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I. INTRODUCTION

Perovskite-type oxides, the chemical formula of which is ABO_3, with transition-metal ions at the B site have been investigated in order to understand the interactions of d electrons in the BO_6 octahedra network connected by the apical oxygen atoms with a ~180° B-O-B bond angle. Particularly, the oxides with quarter-filled $3d$-e_g orbitals have attracted much studies, because the degree of freedom to occupy one of the twofold-degenerate e_g orbitals is connected with some interesting physical properties, such as the Jahn-Teller effect, orbital ordering, metallicity, and ferromagnetism.

The $t_{2g}^3e_g^1$ system has been widely investigated for an insulating $LaMnO_3$.[1–6] The cooperative Jahn-Teller effect occurs at around 750 K accompanied by the characteristic ordering of occupied d_{x^2} and d_{y^2} orbitals.[2] The Curie-Weiss temperature of $LaMnO_3$ is positive in spite of the antiferromagnetic ground state,[1,2] which has been understood by the anisotropic superexchange interaction due to the orbital ordering; ferromagnetic layers are coupled antiferromagnetically. Zhou *et al.* suggested that a long-range ferromagnetic order appears when the occupied e_g orbitals are arranged in a disordered fashion as demonstrated in $LaMn_{1-x}Ga_xO_3$.[3] It is well known that the real charge transfer between Mn^{3+} and Mn^{4+} ions induces ferromagnetism and metallicity based on the double-exchange mechanism when holes are introduced into e_g orbitals, such as $La_{1-x}Sr_xMnO_3$.[4–6] Zhou *et al.* also suggested that the double-exchange interaction acts even in nondoped $LaMnO_3$ above the orbital ordering temperature.[2]

A metallic $SrFeO_3$ has been investigated as another $t_{2g}^3e_g^1$ system.[7–10] The Curie-Weiss temperature of $SrFeO_3$ is also positive in spite of the helical antiferromagnetic ground state,[9] which has been understood by the coexistence of a nearest-neighbor ferromagnetic interaction and long-range antiferromagnetic interaction. In spite of the quarter-filled e_g orbitals, $SrFeO_3$ does not show Jahn-Teller distortion, which has been understood by the itinerant nature of e_g electrons accommodated in a σ^* band formed between Fe e_g and O $2p$ orbitals or by the ground state dominated by a $d^5\underline{L}$ configuration instead of a d^4 configuration, where $\underline{L}$ is the oxygen hole state.[10,23] The $t_{2g}^6e_g^1$ system has been investigated for $L\underline{L}NiO_3$ (L, rare-earth element).[11–16] $LaNiO_3$ is a metallic Pauli paramagnet with enhanced magnetic susceptibility.[11–13] No Jahn-Teller distortion exists in $LaNiO_3$. The other $L\underline{L}NiO_3$ are insulating antiferromagnets with a complex spin arrangement.[14–16] Though the deformation parameter of NiO_6 octahedra (defined as the standard deviation of six Ni-O bond lengths) increases as the size of L^{3+} ions decreases in the insulating $L\underline{L}NiO_3$, the deformation parameter is about 30 times smaller than that of $LaMnO_3$.[16] Recently, Potze *et al.* suggested that trivalent and tetravalent Co ions are other candidates for the ion with quarter-filled e_g orbitals in spite of their $3d^6$ and $3d^5$ configurations,[17] which is connected with the ferromagnetism in $SrCoO_3$.[18] The electronic configurations having one e_g electron and t_{2g} holes, $t_{2g}^5e_g^1$ and $t_{2g}^4e_g^1$, are termed as an intermediate-spin state. In addition to $SrCoO_3$,[17–19] solid solutions including Co ions, $SrFe_{1-x}Co_xO_3$,[20–23] $Sr_{1-x}La_xCoO_3$,[24–26] and $LaCo_{1-x}Ni_xO_3$,[27–32] show metallicity and ferromagnetism in a certain x range.

It has been considered that the small or negative charge transfer energy from oxygen to transition-metal ions is important for the metallicity in the above oxides $SrFeO_3$, $SrFe_{1-x}Co_xO_3$, $SrCoO_3$, $Sr_{1-x}La_xCoO_3$, $LaCo_{1-x}Ni_xO_3$, and $LaNiO_3$, because the $3d$ level of highly oxidized transition-metal ions, such as Fe^{4+}, Co^{4+}, Co^{3+}, and Ni^{3+}, is deep and close to the O^{2-} $2p$ level. However, the origin of the magnetic interaction in these metallic oxides has not yet been clarified as compared to manganese oxides. The metallic oxides including Co ions show ferromagnetism, in spite of the different number of $3d$ electrons between 4 and 7. Thus, the clarification of the relation of ferromagnetism to

the presence or absence, valence, and spin state of Co ions should provide a clue to understand the origin of magnetic interaction in the metallic oxides. The present study investigated $LaCo_{0.5}Ni_{0.5}O_3$ because of the lack of systematic studies regarding it, particularly valence and spin states. In addition, we discuss the origin of the ferromagnetism appearing in the metallic oxides with $3d$ electrons between 4 and 7.

II. EXPERIMENT

$LaCoO_{3-\delta}$ and $LaCo_{0.5}Ni_{0.5}O_{3-\delta}$ were prepared by a solid-state reaction method from La_2O_3, NiO, and $CoC_2O_4 \cdot 2H_2O$. The mixed powder was calcined in air at 1273–1473 K, pressed into pellets, and sintered in air at 1473–1573 K for 12 h. $LaNiO_{3-\delta}$ was prepared by a precursor method using citric acid from La_2O_3 and Ni. The precursor was fired at 1073 K for 24 h. Iodometric titration and thermogravimetric analyses determined the oxygen deficiency, -0.02, -0.01, and 0.1 within the experimental error ± 0.02 for $LaCoO_{3-\delta}$, $LaCo_{0.5}Ni_{0.5}O_{3-\delta}$, and $LaNiO_{3-\delta}$, respectively. The prepared $LaCoO_{3-\delta}$ and $LaNiO_{3-\delta}$ and commercial CoO and NiO were used for the references of x-ray-absorption near-edge structure (XANES).

Powder x-ray diffraction (XRD) measurements using Cu $K\alpha$ radiation (MAC Science, MXP18HF) clarified that the samples are single phase with a rhombohedral unit cell. All the detected diffraction peaks were consistent with the space group $R\bar{3}c$. Lattice parameters of $LaCo_{0.5}Ni_{0.5}O_3$ and $LaNiO_3$ were determined in air in the range 27–1220 K and 420–1220 K, respectively, from some high-angle diffraction peaks using Si crystalline powder as an internal standard. The XRD pattern and the lattice parameters at room temperature did not change before and after the sample was heated to 1220 K. This indicates neither appreciable oxidation of Si nor chemical reaction of Si with the sample up to 1220 K during the measurement period. Structural parameters of $LaNiO_3$, $LaCo_{0.5}Ni_{0.5}O_3$, and $LaCoO_3$ at around 30 K were determined by Rietveld refinements using RIETAN-2000.[33] XANES was measured at room temperature (RIGAKU, R-XAS Looper). dc magnetizations were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5S) in the range 5–300 K and using a magnetic balance (Shimadzu, MB-1A) in the range 300–1100 K. ac magnetic susceptibilities, dc resistivities, and heat capacities were measured in the range 2–200 K (Quantum Design, PPMS). Thermogravimetric analysis was carried out in the range 300–1273 K (MAC Science, 2000S).

III. RESULTS

Figures 1(a) and 1(b) show Co K-edge and Ni K-edge XANES, respectively, at room temperature. The Co K and the Ni K absorption edges of $LaCo_{0.5}Ni_{0.5}O_3$ are close to those of $LaCoO_3$ and $LaNiO_3$ and clearly higher than those of CoO and NiO, respectively. It concludes that both valences of Co and Ni ions in $LaCo_{0.5}Ni_{0.5}O_3$ are trivalent at least at room temperature.

Structural parameters at around 30 K determined by

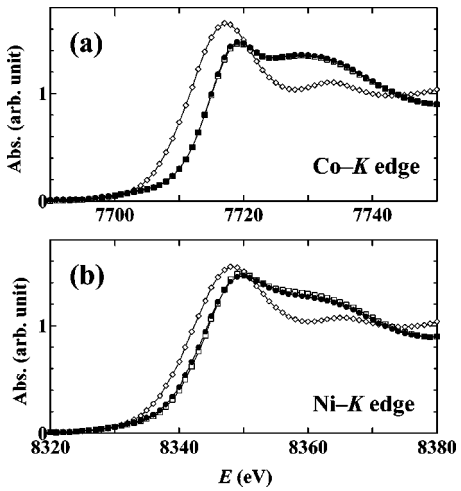

FIG. 1. (a) Co K-edge XANES: ●, $LaCo_{0.5}Ni_{0.5}O_3$; □, $LaCoO_3$; ◇, CoO. (b) Ni K-edge XANES: ●, $LaCo_{0.5}Ni_{0.5}O_3$; □, $LaNiO_3$; ◇, NiO.

Rietveld refinements and reliability factors for the fitting are tabulated in Table I. The composition x dependence of the unit-cell volume, B-O bond length, and B-O-B bond angle of $LaCo_{1-x}Ni_xO_3$ (B=Co, Ni) are shown in Figs. 2(a), 2(b), and 2(c), respectively. The literature values (open circles) determined by neutron diffraction are plotted for $LaCoO_3$ at 31 K (Ref. 34) and $LaNiO_3$ at 30 K (Ref. 14) together with the present data (solid circles). (The literature values of $LaCoO_3$ at 31 K were estimated by interpolating the data at 4 and 71 K.) The present data are coincident with the literature data within the fitting error, which ensures the accuracy of the present data. The unit cell volume and the B-O bond length are largest and the B-O-B bond angle is smallest at $x=0.5$. The largest B-O bond length at $x=0.5$ indicates that the average size of B-site ions in $LaCo_{0.5}Ni_{0.5}O_3$ is larger than that of either Co ions in $LaCoO_3$ or Ni ions in $LaNiO_3$. In addition, the B-O-B bond angle being smallest at $x=0.5$ is also understood by the decreased tolerance factor $t=(r_{La^{3+}}+r_{O^{2-}})/\sqrt{2}(r_{B^{3+}}+r_{O^{2-}})$, which increases the tilt angle of the BO_6 octahedron, where r_M is the radius of the M ion.

Figure 3(a) shows the temperature dependence of the unit-

TABLE I. Structural parameters of $LaCo_{1-x}Ni_xO_3$ determined by Rietveld refinement with the space group $R\bar{3}c$. Isotropic temperature factors of La, B (=Co, Ni), and O were fixed at 0.1, 0.1, and 0.2, respectively.

x	0	0.5	1
T (K)	31	27	33
a (Å)	5.4250(5)	5.4620(6)	5.451(2)
c (Å)	13.0065(8)	13.077(1)	13.115(2)
V (Å^3)	331.51(5)	337.86(6)	337.4(1)
x[O]	0.5529(6)	0.5543(5)	0.5462(6)
$d_{B\text{-}O}$ (Å)	1.9260(7)	1.9394(6)	1.9323(9)
$\theta_{B\text{-}O\text{-}B}$ (deg)	162.9(2)	162.5(2)	165.0(2)
R_{wp} (%)	13.15	10.75	10.41
R_I (%)	3.82	5.83	1.37

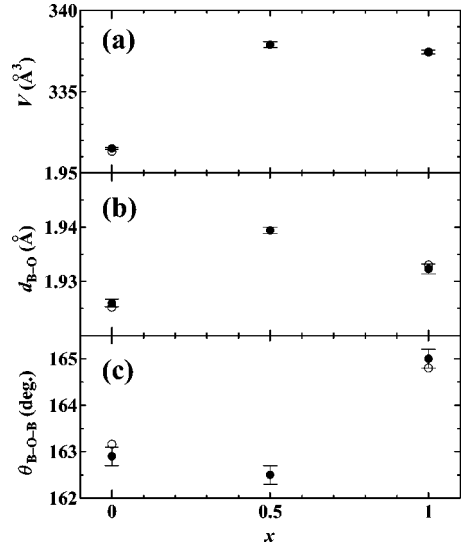

FIG. 2. Composition dependences of (a) unit-cell volume, (b) B-O bond length, and (c) B-O-B bond angle of $LaCo_{1-x}Ni_xO_3$ around 30 K: ●, present data (Table I); ○, literature data (Refs. 14 and 34).

cell volume of $LaCo_{0.5}Ni_{0.5}O_3$, $LaCoO_3$,[34] and $LaNiO_3$.[14] Thermogravimetric analysis of $LaCo_{0.5}Ni_{0.5}O_3$ confirmed that the evolution of oxygen from the sample is at most $\delta = 0.01$ between room temperature and 1273 K. The thermal expansion of $LaCoO_3$ between 0 and ~1200 K is about twice as large as that of $LaNiO_3$. The large thermal expansion of $LaCoO_3$ has been attributed to the spin-state transition of trivalent Co ions from the low-spin state to the high- or intermediate-spin state.[35] The thermal expansion and the unit-cell volume of $LaCo_{0.5}Ni_{0.5}O_3$ are very close to those of $LaNiO_3$ below room temperature. This implies that the spin state (and the valence) does not change appreciably below room temperature. The thermal expansion of $LaCo_{0.5}Ni_{0.5}O_3$ becomes larger than that of $LaNiO_3$ above room temperature and the unit-cell volume is between those of $LaCoO_3$ and $LaNiO_3$ above 600 K.

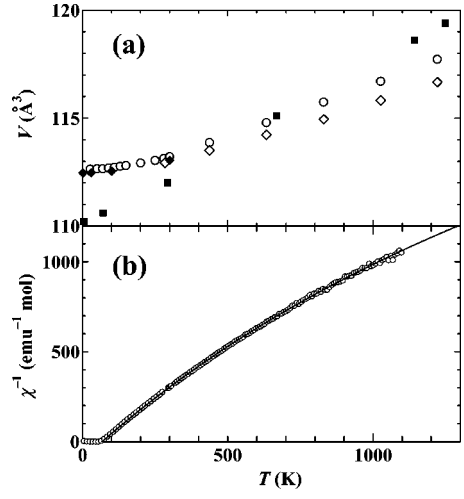

FIG. 3. (a) Temperature dependences of the unit-cell volume: ○, $LaCo_{0.5}Ni_{0.5}O_3$ (present data); ◇, $LaNiO_3$ (present data); ■, $LaCoO_3$ (Ref. 34); ◆, $LaNiO_3$ (Ref. 14). (b) Temperature dependence of the reciprocal magnetic susceptibility of $LaCo_{0.5}Ni_{0.5}O_3$. A solid line is the result of fitting using Eq. (1).

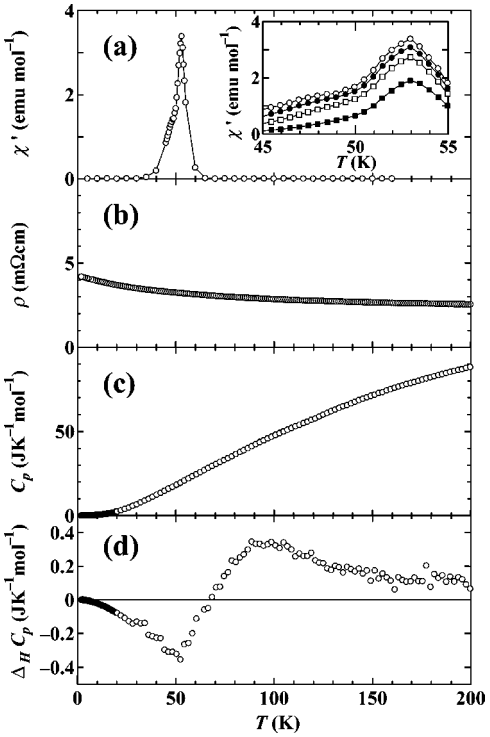

FIG. 4. (a) Real parts of the ac magnetic susceptibility: ○, 10 Hz; ●, 100 Hz; □, 1 kHz; ■, 10 kHz, (b) resistivity, (c) heat capacity: ○, 0 Oe; ●, 90 kOe, and (d) $\Delta_H C_p = C_p(90\ \text{kOe}) - C_p(0\ \text{Oe})$ of $LaCo_{0.5}Ni_{0.5}O_3$.

Figure 3(b) shows the temperature dependence of the reciprocal magnetic susceptibility of $LaCo_{0.5}Ni_{0.5}O_3$. The temperature-independent diamagnetic contribution due to the core electrons, -6.58×10^{-5} emu mol^{-1}, has already been subtracted from the raw data. The upward convex χ^{-1}-T curve was well reproduced by the equation

$$\chi = \frac{C}{T-\theta} + \chi_0 \tag{1}$$

as indicated by the solid line in the figure which was obtained by the least-squares fitting of the data above 100 K. The best-fit parameters are $C = 0.71(4)$ emu mol^{-1} K [corresponding to $\mu_{\text{eff}} = 2.4(1)\mu_B$], $\theta = 67(4)$ K, and $\chi_0 = 2.6(1)\times10^{-4}$ emu mol^{-1}. Vasanthacharya *et al.* have suggested the ferrimagnetic ordering in $LaCo_{0.5}Ni_{0.5}O_3$ based on the upward convex character of χ^{-1}-T curve.[28] However, the fact that the χ^{-1}-T curve is well reproduced by Eq. (1) in a wide temperature range would reject this suggestion, because the χ^{-1}-T curve of a ferrimagnet should show a sudden bending as the temperature approaches the ordering temperature.

Figure 4(a) shows real parts of the ac magnetic susceptibility of $LaCo_{0.5}Ni_{0.5}O_3$ at 10 Hz. The inset shows the frequency dependence in the temperature range 45–55 K. A peak and a shoulder were observed at 53 K and around 48 K,

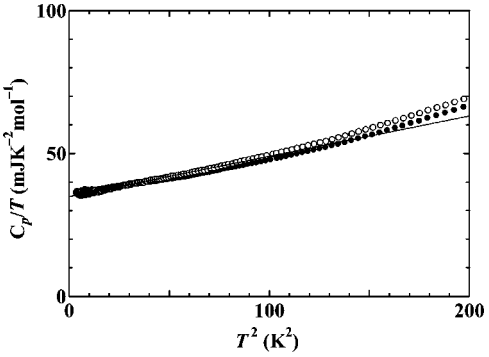

FIG. 5. C_p/T vs T^2 plot of $LaCo_{0.5}Ni_{0.5}O_3$: ○, 0 Oe; ●, 90 kOe. A solid line is the result of fitting using Eq. (2).

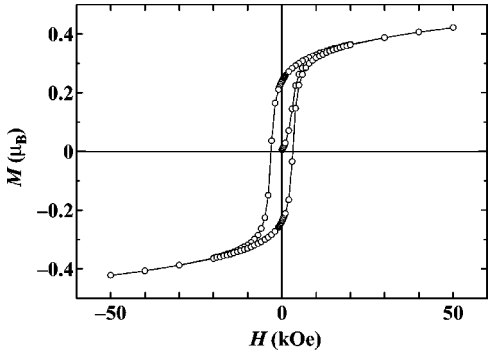

FIG. 6. M vs H plot of $LaCo_{0.5}Ni_{0.5}O_3$ at 5 K.

respectively. The peak temperature does not appreciably depend on the frequency while the peak magnitude depends on the frequency. The resistivity shown in Fig. 4(b) is on the order of 10^{-3} Ω cm and slightly increases with decreasing temperature, having a temperature derivative much smaller than that of a semiconductor. No appreciable anomaly was observed in the resistivity around 50 K. The open and solid circles in Fig. 4(c) represent heat capacities of $LaCo_{0.5}Ni_{0.5}O_3$ under 0 and 90 kOe, respectively. Because of the similar value, the data are superimposed. Figure 4(d) shows $\Delta_H C_p = C_p(90\ \text{kOe}) - C_p(0\ \text{Oe})$, where $C_p(H)$ is the heat capacity measured under a magnetic field H. A clear cusp was observed in $\Delta_H C_p$ at around 53 K corresponding to the peak in ac magnetic susceptibility. In addition to this, the absence of an appreciable frequency dependence in the ac susceptibility peak temperature suggests the presence of a critical ferromagnetic ordering temperature at 53 K. On the other hand, no appreciable anomaly was observed around 48 K corresponding to the shoulder seen in the ac magnetic susceptibility. In the light of the lack of a connection between the entropy and shoulder, the magnetic anomaly around 48 K might be connected to the freezing of magnetic domains.

Open and solid circles in Fig. 5 represent the C_p/T vs T^2 plot of $LaCo_{0.5}Ni_{0.5}O_3$ under 0 and 90 kOe, respectively. No appreciable difference was observed below ~7 K between 0 and 90 kOe. This implies that the contribution from the ferromagnetic spin-wave excitation is small even if present possibly because of the large energy gap. Therefore, the low-temperature heat capacity is expressed by

$$C_p = \gamma T + \beta T^3. \tag{2}$$

The best-fit parameters obtained from the data below 7 K under zero field are $\gamma = 34.9(7)\ \text{mJ K}^{-2}\,\text{mol}^{-1}$ and $\beta = 0.141(3)\ \text{mJ K}^{-4}\,\text{mol}^{-1}$. The magnitudes of γ and β are similar to those of a metallic ferromagnet $La_{1-x}Sr_xCoO_3$,[26] but smaller than that of $LaNiO_3$.[12] The magnitude of resistivity was on the order of metal while the temperature derivative of the resistivity was negative as shown in Fig. 4(b). The presence of electronic specific heat clarified the metallicity. This is the same conclusion as that of the literature.[29]

Figure 6 shows the M vs H plot at 5 K measured after zero-field cooling. The magnetization does not saturate even at 50 kOe. Taking account of this, the shoulder in ac susceptibility around 48 K, and the small heat capacity anomaly at 53 K, the presence of a glasslike component is supposed as suggested by Asai *et al.*[27] However, the reverse of magnetization at the coercive force around ±5 kOe is relatively sharp as compared to a spin-glass system. This implies the presence of ferromagnetic domains large enough to include domain walls, even if a glasslike component coexists. The magnetization at 50 kOe is much smaller than the effective magnetic moment $2.4\mu_B$ estimated by Eq. (1).

IV. DISCUSSION

XANES and the unit-cell volume clarified that a 1:1 solid solution of $LaCoO_3$ and $LaNiO_3$ leaves the valences of Co and Ni ions trivalent but expands the average B-O bond length from the average of Co-O bond length in $LaCoO_3$ and Ni-O bond length in $LaNiO_3$. It is thus considered that the solid solution increased the population of e_g orbitals of Co or Ni ions (or σ^* band) from those of $LaCoO_3$ ($t_{2g}^6 e_g^0$) or $LaNiO_3$ ($t_{2g}^6 e_g^1$). We have reported that the spin state of Co ions in $LaCoO_3$ is sensitive to the substitution of Co by another trivalent M ion.[36] In addition, only a low-spin state has been reported for the trivalent Ni ions in perovskite-type oxides as far as we know. Therefore, it is natural to consider that the solid solution changes the spin state of Co ions and leaves the spin state of Ni ions at the low-spin state. This consideration is consistent with our suggestion in the earlier paper:[36] The low-spin state of Co ions in $LaCoO_3$ is unstabilized (stabilized) as compared to the high- or intermediate-spin state when the Co ions are substituted by trivalent M ions with Pauling electronegativity larger (smaller) than that of the Co atom. Considering that Pauling electronegativity increases with the increase in the atomic number from Ti to Cu,[37] the Pauling electronegativity of Ni atoms would be larger than that of Co atoms, though the same values are tabulated for Co and Ni atoms in Pauling's table. Therefore, the substitution of Co^{3+} in $LaCoO_3$ by Ni^{3+} should increase the population of trivalent Co e_g orbitals.

It is difficult to determine the electronic configuration of Co ions in $LaCo_{0.5}Ni_{0.5}O_3$ using the Curie constant, because it is unclear whether the localized picture correctly depicts the ferromagnetism, and the origin of the large χ_0 is undetermined. However, it was found that the unit-cell volume of $LaCo_{0.5}Ni_{0.5}O_3$ is close to (slightly larger than) that of

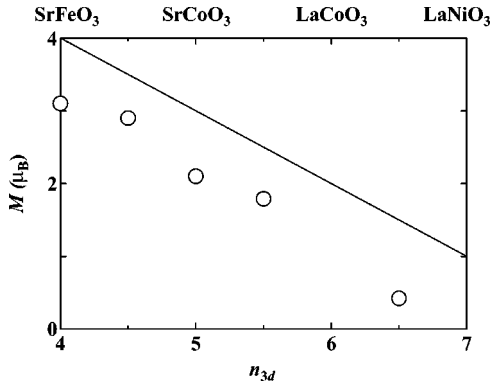

FIG. 7. Magnetization at a high field and a low temperature (open circles) for $SrFe_{0.5}Co_{0.5}O_3$, $SrCoO_3$, $Sr_{0.5}La_{0.5}CoO_3$, and $LaCo_{0.5}Ni_{0.5}O_3$ and the Fe magnetic moment for $SrFeO_3$ estimated by neutron diffraction as a function of the number of $3d$ electrons, n_{3d}. A solid line represents the theoretical magnetization expected from the $t_{2g}^{n_{3d}-1}\sigma^{*1}$ configuration and the full spin polarizations.

$LaNiO_3$ below room temperature. This result indicates that the size of Co ions is similar to that of the low-spin trivalent Ni ion. This rejects at least a possibility of the high-spin state of Co ions, because the ion radius is much larger than that of the low-spin trivalent Ni ion.[38] The intermediate-spin state with $t_{2g}^5 e_g^1$ configuration might be consistent with this result, because the population of e_g orbitals is the same as that of the low-spin trivalent Ni ion, which may give a similar size. The long-range configuration of Ni and Co ions in $LaCo_{0.5}Ni_{0.5}O_3$ would be disordered due to their similar ion sizes. This must be a reason for the glasslike component observed in the present study.

Kobayashi *et al.* have reported that the magnetic and transport properties of $LaCo_{1-x}Ni_xO_3$ are similar to those of $La_{1-x}Sr_xCoO_3$, at least in the La-rich region.[39] They suggested that the substitution of Co by Ni induces a charge transfer from Co^{3+} to Ni^{3+}, resulting in Co^{4+} and Ni^{2+}. However, the present study clarified that such a charge transfer does not occur at least at $x=0.5$. Instead, the present study suggested that the Ni substitution increases the population of Co e_g orbitals as stated above. The same population change has been suggested for $La_{1-x}Sr_xCoO_3$ with increasing x.[26] In addition, the present study clarified that the anomalously large electronic specific heat coefficient of $LaCo_{0.5}Ni_{0.5}O_3$ is comparable to that of $La_{1-x}Sr_xCoO_3$. These results suggest that the structure of the σ^* band and the electronic state, such as the population, density of states at Fermi level, and the electron correlation, are essentially same between $LaCo_{1-x}Ni_xO_3$ and $La_{1-x}Sr_xCoO_3$.

As mentioned in Sec. I, the quarter-filled σ^* band is expected for the electronic structure of $SrFeO_3$, $SrFe_{1-x}Co_xO_3$, $SrCoO_3$, $Sr_{1-x}La_xCoO_3$, $LaCo_{1-x}Ni_xO_3$, and $LaNiO_3$. The open circles in Fig. 7 represent the experimental magnetization at a high field and a low temperature for $SrFe_{0.5}Co_{0.5}O_3$,[22] $SrCoO_3$,[18] $Sr_{0.5}La_{0.5}CoO_3$,[25] and $LaCo_{0.5}Ni_{0.5}O_3$ and the magnetic moment of Fe ions in $SrFeO_3$ estimated by neutron diffraction experiment[9,10] as a function of the number of $3d$ electrons, n_{3d}. The solid line in the figure indicates the theoretical magnetization expected from the $t_{2g}^{n_{3d}-1}\sigma^{*1}$ configuration and the full spin polarizations. The experimental and theoretical magnetizations seem to decrease at a common rate with increasing n_{3d}. This implies that the electrons occupy the minor-spin t_{2g} orbitals instead of the major-spin σ^* band above $n_{3d}=4$. However, the experimental magnetization is about $1\mu_B$ smaller than the theoretical one in each sample. Two possibilities are supposed for the reason why the magnetization at a high field and a low temperature is smaller than the theoretical one. One is that the polarization is incomplete and the other is that some antiferromagnetic interaction coexists with a ferromagnetic one. The latter might be plausible for $LaCo_{0.5}Ni_{0.5}O_3$, because a glasslike component was observed as expected from the chemical disorder at the B site. On the other hand, the latter is not plausible for $SrFeO_3$ and $SrCoO_3$, because chemical disorder is absent. It is thus difficult to conclude which possibility is essential for these metallic materials. This will be clarified by investigating the spin arrangement of each ion using methods such as an x-ray magnetic circular dichroism (XMCD) technique.

The present study clarified that the valence of Co ions is not important for $SrFe_{1-x}Co_xO_3$, $Sr_{1-x}La_xCoO_3$, and $LaCo_{1-x}Ni_xO_3$ showing ferromagnetism, because these oxides formally include only tetravalent, both tetravalent and trivalent, and only trivalent Co ions, respectively. In addition, taking account of the fact that $SrFeO_3$ is essentially a ferromagnet, the presence or absence of Co ions would not be very important for the ferromagnetism. We propose two necessary conditions for the ferromagnetism, t_{2g} holes and itinerant σ^* electrons, based on the following three facts. (1) Though $LaCo_{0.5}Ni_{0.5}O_3$ shows metallicity and ferromagnetism, $NdCo_{0.5}Ni_{0.5}O_3$ shows insulating and spin-glass behaviors.[40,41] In addition, x of the unit-cell volume of $NdCo_{1-x}Ni_xO_3$ shows a linear dependence,[41] which indicates that most Co and Ni ions remain in their low-spin trivalent states. These facts imply a connection among the ferromagnetism, metallicity (itinerant σ^* electrons), and/or t_{2g} holes. (2) $LaNiO_3$ shows no ferromagnetism, which implies a connection between the ferromagnetism and t_{2g} holes. (3) $LaCo_{0.5}Rh_{0.5}O_3$ shows neither metallicity nor ferromagnetism although most trivalent Co ions are not in the low-spin state,[36] which implies a connection between ferromagnetism and metallicity (itinerant σ^* electrons).

V. CONCLUDING REMARKS

In conclusion, the present study clarified that a 1:1 solid solution of $LaCoO_3$ and $LaNiO_3$ leaves the valences of Co and Ni ions trivalent and suggested that the solid solution increases the population of trivalent Co e_g orbitals from $t_{2g}^6 e_g^0$ in $LaCoO_3$. In addition, it was proposed that the electronic configuration of metallic oxides $SrFeO_3$, $SrFe_{1-x}Co_xO_3$, $SrCoO_3$, $Sr_{1-x}La_xCoO_3$, $LaCo_{1-x}Ni_xO_3$, and $LaNiO_3$ is $t_{2g}^{n_{3d}-1}\sigma^{*1}$ and that t_{2g} holes and itinerant σ^* electrons are necessary for the ferromagnetism. The ferromagnetism might originate from a double-exchange interaction similar to $La_{1-x}Sr_xMnO_3$.[4–6] However, the long-range antiferromagnetic interaction present in $SrFeO_3$ (Ref. 9) is different from the characters of $La_{1-x}Sr_xMnO_3$. This inter-

action should be considered carefully in order to clarify whether or not the origin of ferromagnetism is a double-exchange interaction.

Though $LaCo_{0.5}Ni_{0.5}O_3$ is considered to be essentially a metallic ferromagnet, there remain many unresolved issues: these include the origin of large χ_0 and large γ, the fact that the magnetization does not saturate even at 50 kOe and at 5 K, and the reason why the magnetization at 50 kOe is much smaller than the effective magnetic moment. These problems should be clarified in connection with the electronic structure, ferromagnetic domain structure (including glasslike component), and chemical order and disorder.

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[1] G.H. Jonker, Physica (Amsterdam) **22**, 707 (1956).
[2] J.-S. Zhou and J.B. Goodenough, Phys. Rev. B **60**, R15 002 (1999).
[3] J.-S. Zhou, H.Q. Yin, and J.B. Goodenough, Phys. Rev. B **63**, 184423 (2001).
[4] C. Zener, Phys. Rev. **82**, 403 (1951).
[5] P.W. Anderson and H. Hasagawa, Phys. Rev. **100**, 675 (1955).
[6] P.G. de Gennes, Phys. Rev. **118**, 141 (1960).
[7] P.K. Gallagher, J.B. MacChesney, and D.N.E. Buchanan, J. Chem. Phys. **41**, 2429 (1964).
[8] J.B. MacChesney, R.C. Sherwood, and J.F. Poter, J. Chem. Phys. **43**, 1907 (1965).
[9] T. Takeda, Y. Yamaguchi, and H. Watanabe, J. Phys. Soc. Jpn. **33**, 967 (1972).
[10] A.E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, N. Kimizuka, Y. Takeda, and M. Takano, Phys. Rev. B **45**, 1561 (1992).
[11] J.B. Goodenough, N.F. Mott, M. Pouchard, G. Demazeau, and P. Hagenmuller, Mater. Res. Bull. **8**, 647 (1973).
[12] K. Sreedhar, J.M. Honig, M. Darwin, M. McElfresh, P.M. Shand, J. Xu, B.C. Crooker, and J. Spalek, Phys. Rev. B **46**, 6382 (1992).
[13] J.-S. Zhou, J.B. Goodenough, B. Dabrowski, P.W. Klamut, and Z. Bukowski, Phys. Rev. Lett. **84**, 526 (2000).
[14] J.L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre, and J.B. Torrance, Phys. Rev. B **46**, 4414 (1992).
[15] J.L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, Phys. Rev. B **50**, 978 (1994).
[16] J.A. Alonso, M.J. Marínez-Lope, M.T. Casais, J.L. García-Muñoz, and M.T. Fernández-Díaz, Phys. Rev. B **61**, 1756 (2000).
[17] R.H. Potze, G.A. Sawatzky, and M. Abbate, Phys. Rev. B **51**, 11 501 (1995).
[18] P. Bezdicka, A. Wattiaux, J.C. Grenier, M. Pouchard, and P. Hagenmuller, Z. Anorg. Allg. Chem. **619**, 7 (1993).
[19] Y. Takeda, R. Kanno, T. Takada, O. Yamamoto, M. Takano, and Y. Bando, Z. Anorg. Allg. Chem. **540/541**, 259 (1986).
[20] T. Takeda and H. Watanabe, J. Phys. Soc. Jpn. **33**, 973 (1972).
[21] P. Bezdicka, L. Fournes, A. Wattiaux, J.C. Grenier, and M. Pouchard, Solid State Commun. **91**, 501 (1994).
[22] S. Kawasaki, M. Takano, and Y. Takeda, J. Solid State Chem. **121**, 174 (1996).
[23] M. Abbate, G. Zampieri, J. Okamoto, A. Fujimori, S. Kawasaki, and M. Takano, Phys. Rev. B **65**, 165120 (2002).
[24] M. Itoh, I. Natori, I. Kubota, and M. Motoya, J. Phys. Soc. Jpn. **63**, 1486 (1994).
[25] M.A. Señarís-Rodríguez and J.B. Goodenough, J. Solid State Chem. **118**, 323 (1995).
[26] S. Tsubouchi, T. Kyômen, and M. Itoh, Phys. Rev. B **67**, 094437 (2003).
[27] K. Asai, H. Sekizawa, K. Mizushima, and S. Iida, J. Phys. Soc. Jpn. **43**, 1093 (1977).
[28] N.Y. Vasantharya, P. Ganguly, and C.N.R. Rao, J. Solid State Chem. **53**, 140 (1984).
[29] K.P. Rajeev and A.K. Raychaudhuri, Phys. Rev. B **46**, 1309 (1992).
[30] H. Sawada, N. Hamada, and K. Terakura, J. Phys. Chem. Solids **56**, 1755 (1995).
[31] J. Pérez, J. García, J. Blasco, and J. Stankiewicz, Phys. Rev. Lett. **80**, 2401 (1998).
[32] M.T. Escode, C.H. Westphal, and R.F. Jardim, J. Appl. Phys. **87**, 5908 (2000).
[33] F. Izumi and T. Ikeda, Mater. Sci. Forum **321-324**, 198 (2000).
[34] G. Thornton, B.C. Tofield, and A.W. Hewat, J. Solid State Chem. **61**, 301 (1986).
[35] K. Asai, A. Yoneda, O. Yokokura, J.M. Tranquada, G. Shirane, and K. Kohn, J. Phys. Soc. Jpn. **67**, 290 (1998).
[36] T. Kyômen, Y. Asaka, and M. Itoh, Phys. Rev. B **67**, 144424 (2003).
[37] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960).
[38] R.D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).
[39] Y. Kobayashi, S. Murata, K. Asai, J.M. Tranquada, G. Shirane, and K. Kohn, J. Phys. Soc. Jpn. **68**, 1011 (1999).
[40] J. Blasco and J. García, J. Phys. Chem. Solids **55**, 843 (1994).
[41] J. Blasco and J. García, Phys. Rev. B **51**, 3569 (1995).