Magnetic properties of $LaSrCo_{0.5}Ni_{0.5}O_4$

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Abstract

DC magnetization, AC magnetic susceptibility, and heat capacity measurements of polycrystalline $LaSrCo_{0.5}Ni_{0.5}O_4$ conclude that the paramagnetic phase freezes in the spin glass state below about 20 K. It was suggested that the low-spin Co^{III} and Ni^{III} in the ground state are thermally excited to the higher-spin state as the temperature increased.

Key words: spin glass ; spin state ; $LaSrCo_{0.5}Ni_{0.5}O_4$

Perovskite-type oxides $LnCo_{1-x}Ni_xO_3$ (Ln = La, Pr, Nd, and Sm) show ferromagnetic or spin glass behavior[1,2], though $LnCoO_3$'s are diamagnets [3], $LaNiO_3$ is a Pauli paramagnet, and $LnNiO_3$ (Ln = Pr, Nd, and Sm) are antiferromagnets [4]. The magnetic interactions of Co^{3+}-Ni^{3+} or Co^{3+}-Co^{4+} pair (Co^{4+} and Ni^{2+} are produced by charge transfer from Ni^{3+} to Co^{3+}) have been proposed for the origin of ferromagnetic interaction appeared by mixing the Co and Ni oxides [1]. However, there is no decisive evidence for the proposition and the spin states of the ions are unclear. In the present study, the magnetic properties of a layered perovskite-type oxide $LaSrCo_{0.5}Ni_{0.5}O_4$ were investigated in order to obtain a new information on the magnetic interaction and the spin state appeared in the Co and Ni mixed oxide systems.

$LaSrCo_{0.5}Ni_{0.5}O_{4-\delta}$ polycrystalline sample was prepared by a solid-state reaction method. La_2O_3, $SrCO_3$, $CoC_2O_4 \cdot 2H_2O$, and NiO mixed powder was calcined at 1273 K, pressed into pellets, and sintered at 1473 K for 24 h. The powder X-ray diffraction measurements using Cu $K\alpha$ radiation confirmed absence of impurity phase. The diffraction pattern was well-reproduced by Rietveld refinement using RIETAN-2000 program [5] assuming the space group $I4/mmm$. The unit cell parameters, $a = 3.8164(3)$ Å and $c = 12.495(2)$ Å, were determined using Si crystal as an internal standard. The iodometric titrations assuming the stoichiometric metal compositions give δ as 0.01 ± 0.02. The DC magnetizations were measured using a SQUID magnetometer (MPMS5S, Qunatum Design) in the range 5-300 K and a magnetic balance (MB-1A, Shimadzu) in the range 300-1100 K. The AC magnetic susceptibilities were measured with the amplitude 10 Oe using Physical Property Measurement System (PPMS, Quantum Design). The heat capacities were measured by a relaxation method using PPMS.

Open and solid circles in Fig. 1(a) represent the DC magnetizations, M, divided by the applied magnetic field, H, (= 100 Oe) measured on heating the sample after cooling in 100 Oe magnetic field and zero field, respectively, from 300 to 5 K. The difference in magnitude was observed between the field and the zero-field cooling magnetizations below about 20 K. The AC magnetic susceptibilites, as shown in Fig. 1(b), showed a peak around 20 K and the peak temperature decreased as the frequency decreased. On the other hand, no appreciable heat capacity anomaly was observed around 20 K, as shown in Fig. 1(c). Solid circles in Fig. 2 show a M-H curve measured by the sequense that $0 \rightarrow 50 \rightarrow -50 \rightarrow 50$ kOe after zero field cooling from 300 to 5 K. This shows a hysteresis loop. However, the magnetization increases gradually as the field increased and does not saturate even at 50 kOe. Open circles in Fig. 2 show a M-H curve measured by the sequense that $50 \rightarrow -50 \rightarrow 50$ kOe after 50 kOe

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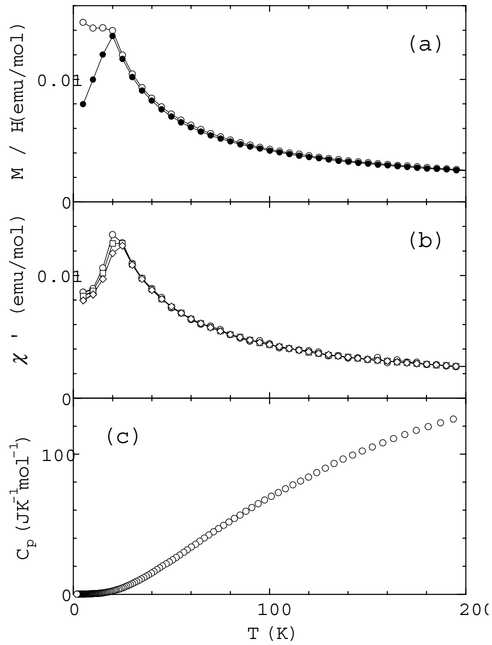

Fig. 1. (a) DC magnetizations divided by the applied magnetic field (100 Oe) measured after zero field (•) and 100 Oe field (∘) cooling. (b) AC magnetic susceptibilities: ∘, 0.1 kHz; □, 1 kHz; ⋄, 10 kHz. (c) heat capacities.

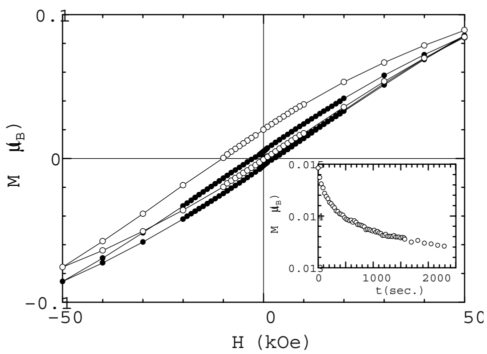

Fig. 2. M-H curves at 5 K measured after zero field (•) and 50 kOe field (∘) cooling. Inset shows the time dependence of magnetization at 5 K measured just after the field was set to and reached at 0 Oe from 50 kOe.

field cooling from 300 to 5 K. This also shows a hysteresis loop, but the center of loop shifted to the positive direction of magnetization. In addition, the magnetization finally measured at 50 kOe is smaller than the value initially measured at 50 kOe. After the M-H loop measurement, the magnetic field was set to zero from 50 kOe and the time dependence of magnetization was measured just after the magnetic field reached at 0 Oe. The measurement showed a relaxation phenomenon (see the inset of Fig. 2). The above magnetic and calorimetric properties conclude that the magnetic

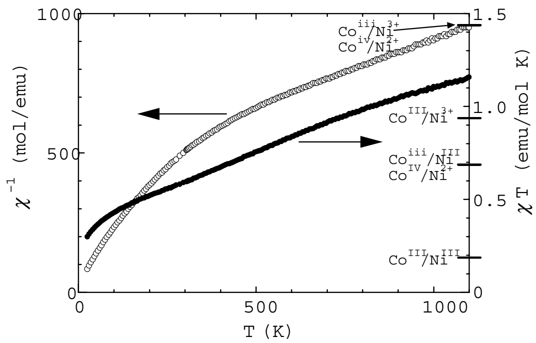

Fig. 3. Inverses of magnetic susceptibility (∘) and magnetic susceptibilities multiplied by the temperature (•). Bars on the right axis represent the Curie constant corresponding to 50:50 cobalt and nickel ions written in the left side (superscript: capital roman, low spin; small roman, intermediate spin; arabic+, high spin).

anomaly at about 20 K is not a phase transition but a freezing-in a spin glass state.

Open circles in Fig. 3 represent the inverses of magnetic susceptibility, χ, above 20 K. The upward convex χ^{-1}-T curve cannot be exactly reproduced by a usual equation, $\chi = \chi_0 + C/(T-\theta)$, implying C depending on T. χ^{-1} seems to tend to about zero as the temperature tends to 0 K. This indicates that θ is nearly zero at least at the low temperatures. Therefore, it is plausible to express that $\chi = \langle C\rangle/T$, where $\langle C\rangle$ is a thermal average of Curie constant. Solid circles in Fig. 3 represent χT. As the temperature decreased, χT seems to tend to 0.19 emu/mol K corresponding to $\langle C\rangle$ of 50:50 low-spin Co^{III} and low-spin Ni^{III}. The presences of flustration and diamagnetic Co^{III} are consistent with the small θ. The increase in χT as the temperature increased implies that the excited states with a higher spin quantum number are populated at high temperatures.

In conclusion, a spin-glass behavior was observed below about 20 K in $LaSrCo_{0.5}Ni_{0.5}O_4$. This indicates the appearance of ferromagnetic ion pair by mixing the Co and Ni parent oxides. In addition, we suggest that the low-spin Co^{III} and/or the low-spin Ni^{III} in the ground state are thermally excited to the higher-spin state.

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