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Magnetic Structures of $La_{1-x}Sr_xCrO_3$ ($x = 0.05$ and 0.15)

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Magnetic properties on perovskite-type compounds $La_{1-x}Sr_xCrO_3$ ($x = 0.05$ and 0.15) have been investigated. From the magnetic susceptibility measurements, three magnetic anomalies have been observed for both $La_{0.95}Sr_{0.05}CrO_3$ (at 21 K, 85 K and 280 K) and $La_{0.85}Sr_{0.15}CrO_3$ (at 26 K, 160 K and 267 K). Powder neutron diffraction measurements were performed for $La_{0.95}Sr_{0.05}CrO_3$ at 10 K, 50 K and 125 K, and for $La_{0.85}Sr_{0.15}CrO_3$ at 10 K, 50 K, 250 K and room temperature. They indicate that the anomalies found for these two compounds at *ca.* 20 K in their susceptibility *vs.* temperature curves are not ascribable to the magnetic transition. The magnetic structures for both the compounds have been determined to be the *G*-type, in which Cr atoms are antiferromagnetically coupled with the six neighboring Cr atoms at any of the temperatures. The magnetic moments of Cr atoms are directed to the *z*-axis of an orthorhombic unit cell for $La_{0.95}Sr_{0.05}CrO_3$ at 10 K and 50 K, and for $La_{0.85}Sr_{0.15}CrO_3$ at 10 K and 50 K; the G_z mode dominates. The G_y mode dominates for $La_{0.95}Sr_{0.05}CrO_3$ at 125 K, *i.e.*, a spin reorientation has occurred between 50 K and 125 K. At 250 K, the crystal structure of $La_{0.85}Sr_{0.15}CrO_3$ is rhombohedral, *i.e.*, a phase transition has occurred between 50 K and 250 K, and the direction of magnetic moments is directed to the [111] of the unit cell.

KEYWORDS: $La_{1-x}Sr_xCrO_3$, magnetic susceptibility, magnetic structure, spin reorientation, heat capacity

§1. Introduction

Lanthanum chromate $LaCrO_3$ is a perovskite-type compound. It is orthorhombic at room temperature, *i.e.*, it has a so-called $GdFeO_3$-type structure with space group *Pnma* (No.62).[1)] At *ca.* 540 K, the $LaCrO_3$ shows an orthorhombic-to-rhombohedral transition.[2,3)] The rhombohedral phase has a $LaAlO_3$-type structure with space group *R*-3*c* (No.167).[4)] This compound shows an antiferromagnetic ordering below 282 K. [5)]

Strontium-substituted $La_{1-x}Sr_xCrO_3$ has recently received much interest as an electrode material or interconnector for fuel cells, heating elements for high-temperature furnaces, *etc.*, because of its high electric conductivity at high temperatures and heat-resistance. [6–10)]

In this study, we prepared $La_{1-x}Sr_xCrO_3$ ($x = 0.05$ and 0.15) and measured their DC magnetic susceptibilities, powder neutron diffraction, heat capacity in order to clarify the magnetic behavior of 3*d* electrons of chromium ions in this system.

§2. Experimental

A specimen $LaCrO_3$ was prepared by the standard solid state reaction. Starting materials were La_2O_3 and Cr_2O_3. They were ground in an agate mortar, pressed into pellets, and fired in air at 1223 K for 12 hours. After cooling, they were reground and fired in air at 1723 K for 20 hours twice. In a similar way, two specimens $La_{1-x}Sr_xCrO_3$ ($x = 0.05$ and 0.15) were prepared by mixing the starting materials, La_2O_3, Cr_2O_3 and $SrCO_3$ and firing in air at 1723 K for 96 hours. After cooling, regrinding the mixtures and refiring them in a flow of oxygen gas at 1723 K for 14 hours were repeated twice.

Powder neutron diffraction patterns were measured with a high resolution powder diffractometer (HRPD) in the JRR-3M reactor (Japan Atomic Energy Research Institute), with Ge (331) monochromator ($\lambda = 1.823$Å). The measurements were made at 10 K, 50 K and 125 K for $La_{0.95}Sr_{0.05}CrO_3$, at 10 K, 50 K, 250 K and room temperature for $La_{0.85}Sr_{0.15}CrO_3$, and at 10 K for $LaCrO_3$.

Magnetic susceptibilities were measured in a magnetic field of 1000G over the temperature range between 4.5 K and 320 K with a SQUID magnetometer (Quantum Design, MPMS-5S).

Heat capacity measurements were performed using a relaxation technique by the commercial heat capacity measuring system (Quantum Design, PPMS) in the temperature range 6-300 K.

§3. Crystal structures

$La_{0.95}Sr_{0.05}CrO_3$ is an orthorhombic with space group *Pnma* in the temperature range from 10 K to room temperature.[11)] On the other hand, the compound $La_{0.85}Sr_{0.15}CrO_3$ at room temperature and at 250 K has a rhombohedral perovskite.[12)] It has an orthorhombic symmetry both at 50 K and 10 K, *i.e.*, the crystal phase transition from orthorhombic (*Pnma*) to rhombohedral (*R*-3*c*) occurs between 50 K and 250 K.

§4. Magnetic Properties

4.1 Magnetic susceptibilities

Temperature dependence of the magnetic susceptibilities for the samples $LaCrO_3$, $La_{0.95}Sr_{0.05}CrO_3$ and

$La_{0.85}Sr_{0.15}CrO_3$ is shown in Fig. 1. It is clear that the substitution of strontium atoms for lanthanum sites greatly affects the magnetic properties of the $LaCrO_3$. In an earlier work, the Néel temperatures for $LaCrO_3$, $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$ are determined to be 286 K, 280 K and 267 K, respectively.[12] Compared with the susceptibilities for $LaCrO_3$, dramatic differences between ZFC and FC susceptibilities have been observed below Néel temperatures for these Sr-substituted compounds.

Below the Néel temperatures, other two magnetic anomalies have been observed for the Sr-substituted compounds. For $La_{0.95}Sr_{0.05}CrO_3$, one of the anomalies occurs at 85 K, and the other magnetic anomaly is found at 21 K. For $La_{0.85}Sr_{0.15}CrO_3$, the magnetic anomalies occur at 160 K and at 26 K.

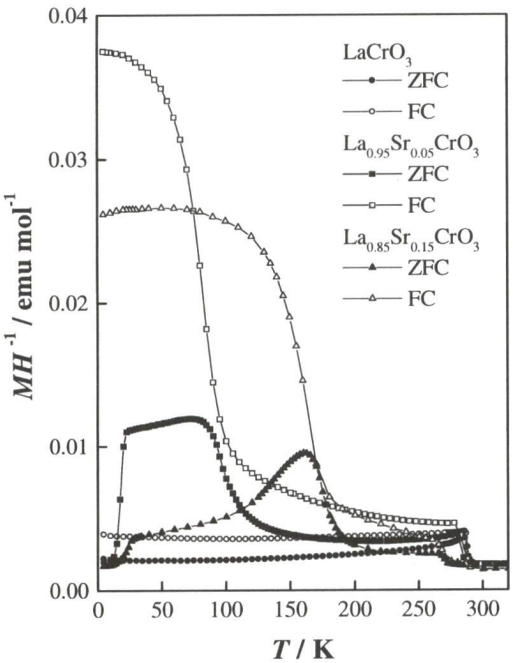

Fig. 1. Temperature dependence of magnetic susceptibilities for $La_{1-x}Sr_xCrO_3$ ($x = 0$, 0.05 and 0.15) measured after zero field cooling (ZFC) and field cooling (FC).

4.2 Magnetic structures

4.2.1 $La_{0.95}Sr_{0.05}CrO_3$

For $La_{0.95}Sr_{0.05}CrO_3$, all the observed magnetic Bragg peaks can be indexed in the crystallographic unit cell, with both $h + l$ and k odd. From the selection rules for the magnetic reflections,[13] the type of magnetic structure has been determined at any temperature to be the G-type, in which Cr atoms are antiferromagnetically coupled with the six neighboring Cr atoms. The magnetic moment of Cr atoms is directed to the z-axis; the G_z mode dominates for the magnetic structure of $La_{0.95}Sr_{0.05}CrO_3$ both at 10 K and at 50 K (see Fig. 2). Neutron diffraction measurements on $La_{0.95}Sr_{0.05}CrO_3$ show that there is no difference between the profiles measured at 10 K and at 50 K, although magnetic anomaly has been found at 21 K in its susceptibility *vs.* temperature curve. Our analysis on the neutron diffraction measurements shows that for $LaCrO_3$ the direction of the magnetic moment of Cr atoms at 10 K is parallel to the x-axis. This result is completely consistent with that reported before.[14] It is interesting that the direction of the magnetic moment is different between $La_{0.95}Sr_{0.05}CrO_3$ (G_z mode) and $LaCrO_3$ (G_x mode).

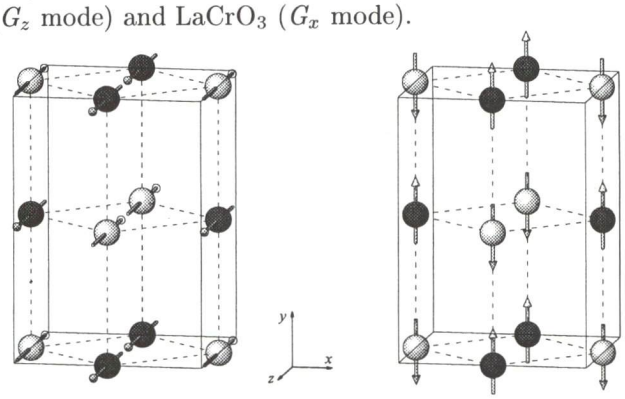

Fig. 2. Magnetic structures for $La_{0.95}Sr_{0.05}CrO_3$: (a) G_z mode (at 10 K and 50 K); (b) G_y mode (at 125 K).

The Rietveld analysis for the intensity data collected at 125 K indicates that the magnetic moment is directed not to the z-axis, but to the y-axis, *i.e.*, the spin reorientation from G_z mode (at 50 K) to G_y mode (at 125 K) has occurred with increasing temperature.

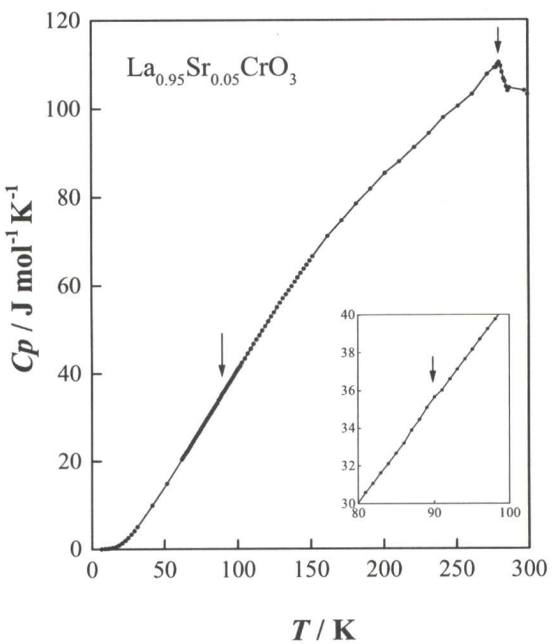

Fig. 3. Temperature dependence of the heat capacities of $La_{0.95}Sr_{0.05}CrO_3$. The arrows indicate the temperatures at which anomalies have been found.

Figure 3 shows the temperature dependence of the heat capacities for $La_{0.95}Sr_{0.05}CrO_3$, indicating the existence of two anomalies at 90 K and 280 K. These are corresponding to the magnetic transitions found in the

magnetic susceptibility *vs.* temperature curve and their magnetic structures have been determined by the neutron diffraction measurements as described above. No heat capacity anomaly has been found at *ca.* 20 K, although magnetic anomaly has been found at 21 K in the susceptibility *vs.* temperature curve. This result is consistent with the results by the neutron diffraction experiments. The anomaly observed at *ca.* 20 K in the susceptibility *vs.* temperature curve may be due to the weakness of the magnetic anisotropy with increasing temperature.

4.2.2 $La_{0.85}Sr_{0.15}CrO_3$

Although the crystal structure changes between these two temperatures, the magnetic structures at 250 K and 50 K are both the *G*-type. At 250 K the magnetic moments of Cr atoms are directed to the [111] of a rhombohedral unit cell, and they are directed to the *z*-axis of an orthorhombic unit cell at 50 K. As shown in Fig. 1, this compound also shows a very steep rise of its susceptibility when the temperature is increased through 26 K. The present neutron diffraction measurements at 10 K show that the magnetic structure is the *G*-type and the magnetic moments of Cr atoms are parallel to the *z*-axis, which is the same as the results at 50 K. Table I summarizes the results of the magnetic structures for $La_{1-x}Sr_xCrO_3$ ($x = 0$, 0.05, and 0.15).

Table I. The magnetic structures for $La_{1-x}Sr_xCrO_3$ ($x = 0$, 0.05 and 0.15) at various temperatures.

	10 K	50 K	125 K(250 K)	RT
$LaCrO_3$	G_x			paramagnetic
$La_{0.95}Sr_{0.05}CrO_3$	G_z	G_z	G_y(125 K)	paramagnetic
$La_{0.85}Sr_{0.15}CrO_3$	G_z	G_z	G^*(250 K)	paramagnetic

*The magnetic moment is directed to the [111] of the rhombohedral unit cell.

Figure 4 shows the temperature dependence of the heat capacity of $La_{0.85}Sr_{0.15}CrO_3$. The heat capacity anomaly has been measured at 160 K, 190 K and 266 K. The anomaly found at 266 K corresponds to the magnetic transition (paramagnetic-antiferromagnetic). The anomaly observed at 190 K seems to correspond to the orthorhombic-to-rhombohedral phase transition. The anomaly at 160 K may indicate the occurrence of the same spin reorientation as found in the $La_{0.95}Sr_{0.05}CrO_3$ at 90 K, because the behavior of the magnetic susceptibility *vs.* temperature curve for $La_{0.85}Sr_{0.15}CrO_3$ around 160 K is quite similar to that for $La_{0.95}Sr_{0.05}CrO_3$ around 90 K. Although the magnetic anomaly has been observed at 26 K in the susceptibility vs. temperature curve, no heat capacity anomaly is found. This result is consistent with the results by the neutron diffraction measurements, and this is the same case as for $La_{0.95}Sr_{0.05}CrO_3$ at *ca.* 20 K.

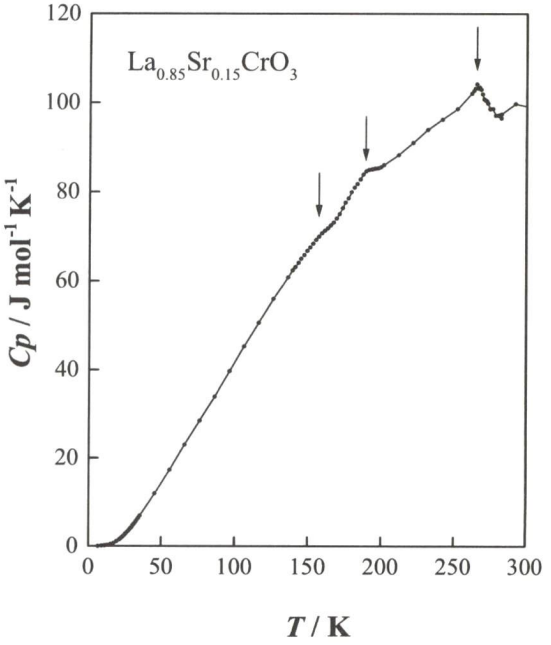

Fig. 4. Temperature dependence of the heat capacities of $La_{0.85}Sr_{0.15}CrO_3$. The arrows indicate the temperatures at which anomalies have been found.

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