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Studies on magnetic properties of La_{0.95}Sr_{0.05}CrO₃ and La_{0.85}Sr_{0.15}CrO₃ by means of powder neutron diffraction

Keitaro Tezuka[†], Yukio Hinatsu[†], Kenichi Oikawa[‡], Yutaka Shimojo[‡] and Yukio Morii[‡]

† Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

‡ Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-1195, Japan

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Abstract. The magnetic properties of the perovskite-type compounds $La_{1-x}Sr_xCrO_3$ (x = 0.05 and 0.15) have been investigated. In the magnetic susceptibility measurements, three magnetic anomalies have been observed for $La_{0.95}Sr_{0.05}CrO_3$ (at 21 K, 85 K and 280 K) and for $La_{0.85}Sr_{0.15}CrO_3$ (at 26 K, 160 K and 267 K). Powder neutron diffraction measurements on these two compounds indicate that the anomaly found at ≈ 20 K in their susceptibility–temperature curves is not ascribable to the magnetic transition. Heat capacity measurements also show that two anomalies have been found at 90 K and 280 K for $La_{0.95}Sr_{0.05}CrO_3$ and at 160 K, 190 K and 266 K for $La_{0.85}Sr_{0.15}CrO_3$, and no anomaly has been found at ≈ 20 K. The magnetic structures for all the compounds have been determined to be of G type, in which Cr atoms are antiferromagnetically coupled with the six neighbouring Cr atoms at all of the temperatures. The magnetic moments of Cr atoms are directed parallel 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 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.

1. Introduction

Lanthanum chromate LaCrO₃ is a perovskite-type compound. It is orthorhombic at room temperature, i.e., it has a so-called GdFeO₃-type structure with space group *Pnma* (No 62) [1]. At \approx 540 K, this LaCrO₃ shows an orthorhombic-to-rhombohedral transition [2]. The rhombohedral phase has a LaAlO₃-type structure with space group $R\bar{3}c$ (No 167) [3]. The oxidation state of chromium in the LaCrO₃ is trivalent. Its electronic structure is [Ar]3d³; LaCrO₃ is paramagnetic. This compound shows an antiferromagnetic ordering below 282 K [4].

Strontium-substituted $La_{1-x}Sr_xCrO_3$ has recently aroused much interest as a possible electrode material or heating element for high-temperature furnaces, etc [5–7]. Although much research on the thermodynamics and conductivity of these compounds has been reported, little is known about their physico-chemical properties at low temperatures.

In an earlier work, magnetic properties of the perovskite-type compounds $La_{1-x}Sr_xCrO_3$ (x = 0, 0.05, 0.10, 0.15, 0.20 and 0.25) have been reported [8]. Their magnetic susceptibilities were measured from 4.5 K to 320 K. Each of these compounds showed an antiferromagnetic transition and their Néel temperatures decreased linearly with increasing Sr substitution. Below the Néel temperatures, two other magnetic transitions were furthermore

4152 K Tezuka et al

observed for almost all the compounds. One of the transitions occurred at a temperature between 50 K and 250 K. The other magnetic transition was found at ≈ 20 K. This transition temperature was independent of the strontium concentration of the compounds. Below the Néel temperatures, all the compounds except for LaCrO₃ showed magnetic hysteresis.

Among these solid solutions, the magnetic behaviour of two solid solutions, namely $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$, particularly attracts our attention. Although they are both strontium-substituted solid solutions, their crystal structures at room temperature are different: orthorhombic for $La_{0.95}Sr_{0.05}CrO_3$ and rhombohedral for $La_{0.85}Sr_{0.15}CrO_3$ [8]. The results of the magnetic susceptibility measurements show that although the temperature dependences of their magnetic susceptibilities are very different, two other magnetic transitions are observed for both of the compounds below their Néel temperatures and one of the magnetic transitions occurs at the same temperature (≈ 20 K) for both. To understand the magnetic behaviour of these compounds at low temperatures, it is essential to elucidate their magnetic structures.

In this study, we have performed powder neutron diffraction measurements on both $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$ at various temperatures. In addition, magnetic hysteresis measurements in the field range between $-50\,000$ G and $50\,000$ G as well as susceptibility measurements in the temperature range between 4.5 K and 320 K were carried out. Heat capacity measurements were also carried out in the temperature range 6–300 K.

2. Experimental procedure

A specimen of LaCrO₃ was prepared by the standard solid-state reaction. The starting materials were La₂O₃ and Cr₂O₃. Because it is very hygroscopic, La₂O₃ was heated in air at 1073 K for eight hours before use. The materials 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 of La_{1-x}Sr_xCrO₃ (x = 0.05 and 0.15) were prepared by mixing the starting materials La₂O₃, Cr₂O₃ and SrCO₃ and firing in air at 1723 K for 96 hours.

Powder neutron diffraction patterns for $La_{0.95}Sr_{0.05}CrO_3$, $La_{0.85}Sr_{0.15}CrO_3$ and $LaCrO_3$ were measured with a high-resolution powder diffractometer (HRPD) in the JRR-3M reactor (Japan Atomic Energy Research Institute), with a Ge(331) monochromator ($\lambda = 1.823$ Å). The collimators used were 6'-20'-6', and they were placed before and after the monochromator, and between the sample and each detector. The set of 64 detectors and collimators, which were placed every 2.5 degrees, rotate around the sample. 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 LaCrO₃. The crystal and magnetic structures of these compounds were determined by the Rietveld method.

Magnetic susceptibilities were measured in a magnetic field of 1000 G over the temperature range between 4.5 K and 320 K with a SQUID magnetometer (Quantum Design, MPMS-5S). Measurements were carried out under both zero-field-cooled (ZFC) conditions and field-cooled (FC) conditions. The field dependence of the magnetization was measured at several temperatures by changing the magnetic field strength in the range between $-50\,000$ G and 50000 G.

Heat capacity measurements were performed using a relaxation technique with a commercially available heat capacity measuring system (Quantum Design, PPMS) in the temperature range 6–300 K. The sample, in the form of a pellet, was mounted on a thin alumina plate with apiezon for better thermal contact.

3. Results and discussion

3.1. Crystal structures

We have performed neutron diffraction measurements on both $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$ at various temperatures, and the results of the crystal structure analysis by the Rietveld method are listed in table 1. $La_{0.95}Sr_{0.05}CrO_3$ shows no crystal phase transition in the temperature range from 10 K to room temperature. On the other hand, the compound $La_{0.85}Sr_{0.15}CrO_3$ is at room temperature and at 250 K a rhombohedral perovskite [8]. It has an orthorhombic symmetry both at 50 K and 10 K, i.e., the crystal phase transition from orthorhombic (*Pnma*) to rhombohedral ($R\bar{3}c$) occurs between 50 K and 250 K.

3.2. Magnetic properties

3.2.1. Magnetic susceptibilities. The temperature dependences of the magnetic susceptibilities for the samples $LaCrO_3$, $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$ are shown in figure 1. It is clear that the substitution of strontium atoms for lanthanum sites greatly affects the



Figure 1. Temperature dependences of the 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).

K Tezuka et al

4154

Table 1. Crystal and magnetic structures for $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$. Note: the results from the neutron diffraction experiments on $La_{0.85}Sr_{0.15}CrO_3$ at 50 K, 250 K and room temperature have been published in [8].

Atom	Position	x	у	z	$B/\text{\AA}^2$
La _{0.95} Sr	0.05CrO3				
125 K; s	pace group	Pnma (No	62)		
$a = 5.4^{\circ}$	713(1) Å, b	= 7.7483(1) Å, $c = 5.5$	103(1) Å	
$R_{wp} = 2$	$7.72\%, R_I =$	$= 1.77\%, R_F$	s = 1.36%,	$R_e = 6.74\%$	
Magneti	c moment:	$2.67(3) \mu_B$			
Directio	n of momer	nt: <i>b</i> -axis			
La, Sr	4c	0.019(1)	1/4	-0.004(1)	0.17
Cr	4b	0	0	1/2	0.25
O(1)	4c	0.494(1)	1/4	0.064(1)	0.26
O(2)	8d	0.227(1)	0.534(1)	0.228(1)	0.35
50 K; sp	ace group I	Pnma (No 62	2)		
$a = 5.4^{\circ}$	701(1) Å, b	= 7.7478(1) Å, $c = 5.5$	085(1) Å	
$R_{wp} = 2$	$7.45\%, R_I =$	$= 1.50\%, R_F$	r = 1.23%, 1	$R_e = 6.76\%$	
Magneti	c moment:	$2.62(3) \mu_B$			
Directio	n of momer	nt: <i>c</i> -axis			
La, Sr	4c	0.019(1)	1/4	-0.004(1)	0.08
Cr	4b	0	0	1/2	0.21
O(1)	4c	0.494(1)	1/4	0.061(1)	0.20
O(2)	8d	0.226(1)	0.534(1)	0.227(1)	0.34
10 K; sp	ace group I	Pnma (No 62	2)		
$a = 5.4^{\circ}$	701(1) Å, b	= 7.7482(1) Å, $c = 5.5$	083(1) Å	
$R_{wp} = 2$	$7.70\%, R_I =$	$= 1.70\%, R_{F}$	r = 1.27%,	$R_e = 6.74\%$	
Magneti	c moment:	$2.65(3) \mu_B$			
Directio	n of momer	nt: <i>c</i> -axis			
La, Sr	4c	0.019(1)	1/4	-0.004(1)	0.07
Cr	4b	0	0	1/2	0.15
O(1)	4c	0.494(1)	1/4	0.065(1)	0.19
O(2)	8d	0.226(1)	0.534(1)	0.227(1)	0.29
La _{0.85} Sr	0.15CrO3				
10 K; sp	ace group I	P <i>nma</i> (No 62	2)		
a = 5.43	574(1) Å, b	= 7.7299(1)) Å, $c = 5.5$	037(1) Å	
$R_{wp} = 2$	$7.80\%, R_I =$	$= 1.70\%, R_{F}$	r = 1.39%,	$R_e = 5.70\%$	
Magneti	c moment:	$2.51(4) \mu_B$			
Directio	n of momer	nt: <i>c</i> -axis			
La, Sr	4c	0.015(1)	1/4	-0.003(1)	0.13
Cr	4b	0	0	1/2	0.20
O(1)	4c	0.496(1)	1/4	0.060(1)	0.26
O(2)	8d	0.232(1)	0.531(1)	0.233(1)	0.39

magnetic properties of the LaCrO₃. In an earlier work, the Néel temperatures for LaCrO₃, La_{0.95}Sr_{0.05}CrO₃ and La_{0.85}Sr_{0.15}CrO₃ were determined to be 286 K, 280 K and 267 K, respectively [8]. Unlike the case for the susceptibilities for LaCrO₃, dramatic differences between the ZFC and FC susceptibilities have been observed below the Néel temperatures for these Sr-substituted compounds.

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

Measurements of the magnetization of La_{0.95}Sr_{0.05}CrO₃ show that it depends greatly on the applied field at 50 K and 10 K, suggesting the existence of a ferromagnetic component in the magnetic moment of chromium. This is calculated to be $10^{-2} \mu_B/\text{Cr}$ from the magnetization curve. Similar magnetic behaviour has been also found in the magnetization of La_{0.85}Sr_{0.15}CrO₃ [8].

3.2.2. Magnetic structures. Magnetic susceptibility versus temperature curves for LaCrO₃, $La_{0.95}Sr_{0.05}CrO_3$ and $La_{0.85}Sr_{0.15}CrO_3$ show that magnetic transitions occur at various temperatures. In order to determine their magnetic structures, we have performed neutron diffraction measurements on these compounds.

3.2.2.1. $La_{0.95}Sr_{0.05}CrO_3$. In the orthorhombic space group Pnma, with Cr atoms in the 4b Wyckoff positions, four magnetic sites are available in the unit cell, namely:

Position	х	у	z
Cr1	1/2	0	0
Cr2	1/2	1/2	0
Cr3	0	1/2	1/2
Cr4	0	0	1/2

with respective magnetic moments S_1 , S_2 , S_3 and S_4 . Four types of magnetic arrangement are possible [9]:

F:
$$S_1 + S_2 + S_3 + S_4$$

G: $S_1 - S_2 + S_3 - S_4$
C: $S_1 + S_2 - S_3 - S_4$
A: $S_1 - S_2 - S_3 + S_4$.

It is known that for magnetic atoms at the 4b sites, some simple selection rules correspond to the F, G, C and A types of magnetic moment arrangement. 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 [9], the type of magnetic structure has been determined to be at all temperatures G type, in which Cr atoms are antiferromagnetically coupled with the six neighbouring Cr atoms. In order to determine the direction of the magnetic moments at each temperature, we have analysed the intensity of the magnetic reflections. The results show that the magnetic moment of Cr atoms is directed parallel 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 figure 2(a)). 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 a magnetic anomaly has been found at 21 K in its susceptibility versus temperature curve. Our analysis of the neutron diffraction measurements shows that for LaCrO₃ 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 [10]. It is interesting that the directions of the magnetic moments are different for $La_{0.95}Sr_{0.05}CrO_3$ (G_z mode) and LaCrO₃ (G_x mode).

According to the representation theory for *Pnma*, different sets of magnetic modes are possible, i.e., for the irreducible representation Γ_{1g} the G_x , C_y and A_z modes; for Γ_{2g} the C_x ,



Figure 2. Magnetic structures for La_{0.95}Sr_{0.05}CrO₃: (a) the G_z mode (at 10 K and 50 K); (b) the G_y mode (at 125 K).

 G_y and F_z modes; for Γ_{3g} the F_x , A_y and C_z modes; and finally for Γ_{4g} the A_x , F_y and G_z modes [9]. The G_z mode for La_{0.95}Sr_{0.05}CrO₃ belongs to the irreducible representation Γ_{4g} . From magnetization measurements at 10 K and 50 K, we have found that there exists a ferromagnetic component in the magnetic moment of chromium, and the ferromagnetic moment is estimated to be $10^{-2} \mu_B/Cr$ from the hysteresis curve. However, the reflection intensity due to the magnetic diffraction is too small compared with that due to the nuclear diffraction for us to estimate the component of the magnetic moment of F type from this powder neutron scattering pattern. It seems to be most likely that the ferromagnetic component of the magnetic moment (F type) is parallel to the *y*-axis, because the mode F_y , transforming according to the same irreducible representation (Γ_{4g}), is considered. The G_x mode for LaCrO₃ belongs to the representation Γ_{1g} . Therefore, no F-type magnetic structure can coexist with this G-type structure. The experimental result that no magnetic hysteresis has been found for LaCrO₃ is consistent with this.

The Rietveld analysis for the intensity data collected at 125 K indicates that the magnetic moment is directed not parallel to the *z*-axis, but parallel to the *x*-axis or the *y*-axis, and the fitting results indicate that the G_y mode is more appropriate at 125 K. That is, the direction of the magnetic moment of Cr atoms at 125 K is parallel to the *y*-axis (see figure 2(b)). Figure 3 shows the results of the fitting of the low-angle diffraction pattern at 125 K for the two cases, G_z and G_y . Thus, the spin reorientation from the G_z mode (at 50 K) to the G_y mode (at 125 K) has occurred with increasing temperature. The G_z mode at 50 K and the G_y mode at 125 K belong to representations Γ_{4g} and Γ_{2g} , respectively. Similar spin reorientation from Γ_{4g} to Γ_{2g} is found, for example, in YbFeO₃ [11].

Figure 4 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 correspond to the magnetic transitions found in the magnetic susceptibility versus temperature curve, and their magnetic structures have been determined from the neutron diffraction measurements as described above. The anomaly at 90 K (the spin-reorientation temperature) is not as clear as that at 280 K (the



Figure 3. Fittings of the powder neutron diffraction pattern of $La_{0.95}Sr_{0.05}CrO_3$ at 125 K for two cases: (a) the G_z mode; (b) the G_y mode. The calculated and observed patterns are shown by the top solid line and the markers above the peaks, respectively. The vertical marks in the middle show positions calculated for magnetic Bragg reflections. The lower trace is a plot of the difference between the calculated and observed intensities. The reliability factor R_{wp} is calculated to be 7.72% for the G_y mode and it is 8.29% for the G_z mode, which indicates that the G_y mode (figure 2(b)) is more appropriate for the direction of the magnetic moments of chromium atoms in $La_{0.95}Sr_{0.05}CrO_3$ at 125 K.





Figure 4. The 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.

Néel temperature), because the entropy change for spin reorientation is much smaller than that for the paramagnetic-to-antiferromagnetic transition. Thus, the type of phase transition at 90 K cannot be determined. No heat capacity anomaly has been found at \approx 20 K, although a magnetic anomaly has been found at 21 K in the susceptibility versus temperature curve. This result is consistent with the results from the neutron diffraction experiments. The anomaly observed at \approx 20 K in the susceptibility versus temperature curve may be due to the weakness of the magnetic anisotropy for increasing temperature.

3.2.2.2. $La_{0.85}Sr_{0.15}CrO_3$. Next, we consider the magnetic structures for $La_{0.85}Sr_{0.15}CrO_3$. In an earlier work, we determined the magnetic structures of $La_{0.85}Sr_{0.15}CrO_3$ both at 250 K and at 50 K [8]. Although the crystal structure changes between these two temperatures, the magnetic structures at 250 K and 50 K are both of G type, i.e., the magnetic moments of Cr atoms are directed parallel to the [111] direction of a rhombohedral unit cell at 250 K, and are directed parallel to the *z*-axis of an orthorhombic unit cell at 50 K. As shown in figure 1, this compound also shows a very large drop of its susceptibility with decreasing temperature through 26 K. The present neutron diffraction measurements at 10 K show that the magnetic structure is of G type and the magnetic moments of Cr atoms are parallel to the *z*-axis, which

4158

is the same as the results at 50 K. That is, there is no difference in the neutron diffraction profiles between 10 K and 50 K. Table 2 summarizes the results on the magnetic structures for $La_{1-x}Sr_xCrO_3$ (x = 0, 0.05 and 0.15).

	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	Gy (125 K)	Paramagnetic
La _{0.85} Sr _{0.15} CrO ₃	\mathbf{G}_{z}	G_z	G* (250 K)	Paramagnetic

Table 2. The magnetic structures for $La_{1-x}Sr_xCrO_3$ (x = 0, 0.05 and 0.15) at various temperatures.

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

Figure 5 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. LaCrO₃ shows an orthorhombic-to-rhombohedral transition at 526 K and we have found that for $La_{0.95}Sr_{0.05}CrO_3$, its transition temperature decreased to 413 K, from the DTA (differential



Figure 5. The 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.

4160 K Tezuka et al

thermal analysis) measurements [8]. If we assume that the phase transition temperature for $La_{1-x}Sr_xCrO_3$ decreases linearly on substituting Sr atoms for La atoms, it is calculated to be 190 K for $La_{0.85}Sr_{0.15}CrO_3$. The anomaly at 160 K may indicate the occurrence of the same spin reorientation as is found in $La_{0.95}Sr_{0.05}CrO_3$ at 90 K, because the behaviour of the magnetic susceptibility versus 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 a magnetic anomaly was found at 26 K in the susceptibility versus temperature curve, no heat capacity anomaly has been found, which is consistent with the results obtained from the neutron diffraction measurements, and this is also the case for $La_{0.95}Sr_{0.05}CrO_3$ at ≈ 20 K.

4. Conclusions

Three magnetic anomalies have been observed in the curves of magnetic susceptibility versus temperature for both La_{0.95}Sr_{0.05}CrO₃ and La_{0.85}Sr_{0.15}CrO₃. The antiferromagnetic structures have been determined to be of G type. The magnetic moments of Cr atoms for La_{0.95}Sr_{0.05}CrO₃ at 10 K and 50 K and those for La_{0.85}Sr_{0.15}CrO₃ at 10 K and 50 K are G_z modes. The G_y mode dominates for La_{0.95}Sr_{0.05}CrO₃ at 125 K, i.e., a spin reorientation has occurred between 50 K and 125 K. Powder neutron diffraction and heat capacity measurements indicate that the anomaly found at \approx 20 K may be due to the magnetic anisotropy.

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