RAPID COMMUNICATION

Reversal of Magnetization in $La_{0.5}Pr_{0.5}CrO_3$

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It was found that the mixed lanthanide orthochromate $La_{0.5}Pr_{0.5}CrO_3$ exhibits large negative magnetization when its magnetization–temperature (M–T) curves are measured in a FC (field-cooled) mode with low applied fields ($\lesssim 5000$ Oe). The compound shows a canted-antiferromagnetic transition at ~ 261 K and a small peak with a positive sign at ~ 220 K. Below this temperature, M decreases with decreasing temperature, passes through a zero value ($M = 0$) around 163 K (T_{comp}), and continues to decrease steeply until ~ 10 K. The same qualitative behavior was observed also for $La_{1-x}Pr_xCrO_3$ with $0.2 \leq x \leq 0.8$. For $La_{0.5}Pr_{0.5}CrO_3$, the maximum absolute value of M below T_{comp} was ~ 40 times as large as that above T_{comp}. © 2000 Academic Press

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Magnetic properties of perovskite chromates have been studied over these several decades. In $LaCrO_3$ with the orthorhombic perovskite structure at room temperature (space group *Pnma*), the localized Cr^{3+} ($3d^3$) moments magnetically order with a Neel temperature (T_N) of 282 K (G type) (1–5). Because of the antisymmetric Dzyaloshinsky–Moriya interaction, this order is accompanied with the spin canting of the Cr^{3+} moments. Therefore, it is denoted as canted-antiferromagnetism. An isostructural compound $PrCrO_3$ contains a magnetic lanthanide ion Pr^{3+} ($4f^2$). This system shows the same type of magnetic order of the Cr^{3+} moments at $T_N = 238.7$ K (1). At lower temperatures, the Pr^{3+} moments also exhibit magnetic order with the F type magnetic structure (6).

To reveal further variation of their magnetic properties, we have prepared an equimolar solid solution between $LaCrO_3$ and $PrCrO_3$, i.e., $La_{0.5}Pr_{0.5}CrO_3$. It was found that the compound exhibits large negative magnetization when its magnetization–temperature (M–T) curves are measured in a FC (field-cooled) mode with low applied fields ($\lesssim 5000$ Oe), which is an entirely different property from those of the end compounds. This communication briefly reports the results.

The samples have been prepared in air by the solid-state reaction method, as in the preparation for $LnCrO_3$ (Ln, lanthanides) and $La_{1-x}Nd_xCrO_3$ (3–5, 7). The starting materials were La_2O_3 (4N, Soekawa), Pr_2O_3 (3N, Soekawa), and Cr_2O_3 (4N, Soekawa). The initial mixtures were well ground, pelletized, and fired in air at 1100°C for 24–48 h. Then the pellets were ground, pelletized, and fired again in air at 1400°C for 24 h. This firing was repeated twice. The end compounds $LaCrO_3$ and $PrCrO_3$ were also prepared for comparison. For each system, several samples were prepared at the firing temperatures between 1350 and 1500°C and were verified.

They were examined by powder XRD (X-ray diffraction) measurements using $CuK\alpha$ radiation (MAC Science Co., M03XHF[22]) with an angle (2θ) step of 0.04° between $2\theta = 20°$ and 120°. The XRD patterns were verified to consist only of the reaction products and were analyzed by the Rietveld method using the program RIETAN (8). The lattice parameters for the end compounds are close to those previously reported (space group *Pnma*) (1–5, 7): $a = 5.4803(1)$ Å, $b = 7.7597(1)$ Å, $c = 5.5165(1)$ Å, and $V = 234.59(1)$ Å^3 for $LaCrO_3$, and $a = 5.4805(1)$ Å, $b = 7.7153(1)$ Å, $c = 5.4500(1)$ Å, and $V = 230.45(1)$ Å^3 for $PrCrO_3$. Reliability (R) factors and goodness-of-fit (S) indicators are up to 15% and 1.4, respectively. Figure 1 shows the result of the analysis for $La_{0.5}Pr_{0.5}CrO_3$. The patterns could be refined also to *Pnma* where the La^{3+} and Pr^{3+} ions randomly occupy at the same lanthanide site. The lattice parameters are $a = 5.4782(1)$ Å, $b = 7.7404(2)$ Å, $c = 5.4831(2)$ Å, and $V = 232.50(1)$ Å^3. Though only the a-length is slightly shorter than those of the end compounds, the cell volume follows the lanthanide contraction.

dc magnetization measurements were performed with a SQUID magnetometer (Quantum Design MPMS). Magnetization–temperature (M–T) curves were measured
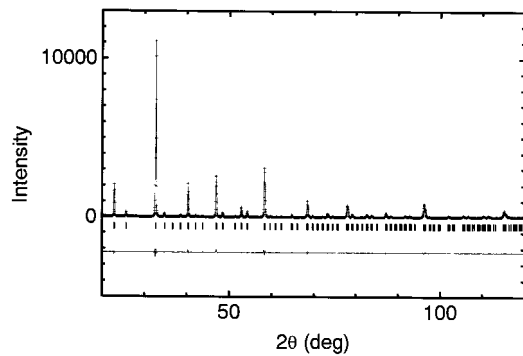
FIG. 1. XRD patterns at room temperature for $La_{0.5}Pr_{0.5}CrO_3$. The observed and calculated patterns are shown as the cross markers and the top solid line, respectively. The vertical markers stand for the angles of Bragg reflections. The lowest solid line represents the difference between the calculated and observed intensities. The fit was done assuming the space group *Pnma*. The parameters obtained are $a = 5.4782(1)$ Å, $b = 7.7404(2)$ Å, $c = 5.4831(2)$ Å, $R_{wp} = 13.52\%$, $R_p = 8.73\%$, goodness-of-fit $(S) = 1.34$, and $R_F = 2.78\%$. The other parameters such as atomic positions are essentially the same as those for $LaCrO_3$ (4).

between 2 and 400 K in field cooled (FC) and zero-field cooled (ZFC) modes with an applied field (H) between 20 and 10,000 Oe. In the former case, measurements were performed on cooling with the field, except for the region of $H \le 1000$ Oe where the measurements both on cooling and heating have been done so far. The results were essentially the same for both processes. dc susceptibilities χ are defined as M/H.

Figure 2 shows the M–T curves for the end compounds, measured with $H = 100$ Oe. The magnetic transitions are observed at $T_N \sim 288$ K and ~ 240 K for $LaCrO_3$ and $PrCrO_3$, respectively, and are close to the values reported previously (1, 4). The deviation between the FC and ZFC curves below T_N for both systems is attributed to the canted-antiferromagnetism. The FC magnetization for $PrCrO_3$ rapidly increases below ~ 70 K, plausibly due to the magnetic order of Pr^{3+} at low temperatures (1, 6).

Figure 3 shows the FC and ZFC M–T curves for $La_{0.5}Pr_{0.5}CrO_3$ with $H = 100$ Oe. A similar transition to those of the end compounds occurs in the FC curve around $T_N \sim 261$ K with a hump of magnetization ($M_P \sim 5$ emu/mol) at $T_P \sim 220$ K (inset). The transition in the ZFC curve is of an analogous shape to that in $LaCrO_3$. Above ~ 300 K, Curie–Weiss (CW) behavior is observed. With further cooling in the FC mode, the magnetization M decreases and passes through a zero value ($M = 0$) around the compensation temperature (T_{comp}) of ~ 163 K. It continues to decrease below T_{comp} until ~ 10 K. The negative values of M indicate that its direction is reverse to that of the applied field. Though the direction of the ZFC magnetization is also opposite to the field (i.e., $M < 0$) below ~ 93 K, its absolute value is much smaller. This phenomenon might be ascribed to random orientation of the magnetic domains.
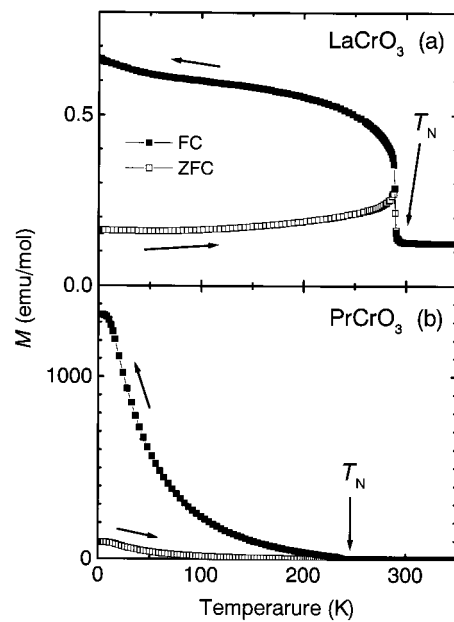

FIG. 2. FC and ZFC M-T curves for (a) $LaCrO_3$ and (b) $PrCrO_3$ with an applied field $H = 100$ Oe.

It is the normal behavior of magnetic materials that the FC magnetization has the same direction as that of the applied field and lies above the ZFC magnetization as seen in Fig. 2. The insulating nature of the system and the much larger absolute values of M below ~ 93 K in the FC curve than those in the ZFC curve exclude the possibility of superconductivity. The curve is almost flattened below ~ 10 K, which might be due to the Pr^{3+} moments (9). The value of M around 2 K is ~ -190 emu/mol, whose absolute value is ~ 40 times as large as M_P. It corresponds to an effective moment of ~ 0.034 μ_B/unit formula. Though the FC curves of $LaCrO_3$ and $PrCrO_3$ were measured with some applied fields between 20 and 10,000 Oe as in Fig. 4 noted below,
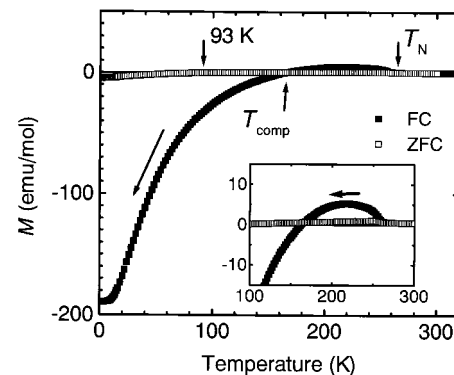

FIG. 3. FC and ZFC M-T curves for $La_{0.5}Pr_{0.5}CrO_3$. The inset shows the temperature region above 100 K for FC curve. See the text for more details.

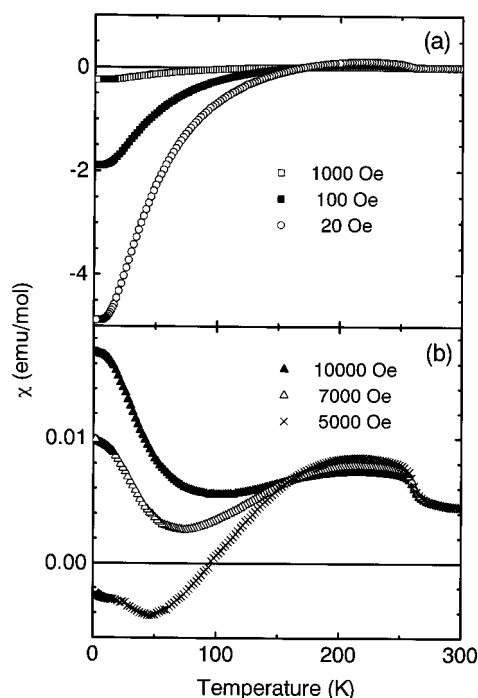**FIG. 4.** FC χ–T curves for $La_{0.5}Pr_{0.5}CrO_3$ with several different applied fields ($\chi = M/H$, M, magnetization; H, applied field).

their profiles were qualitatively identical to those in Fig. 2, and showed no negative magnetization. The measurements were carried out also for Cr_2O_3 to eliminate the possibility that the behavior arises from the starting material. Both as-cast and fired Cr_2O_3 samples exhibited antiferromagnetic transitions at $T_N \sim 310$–320 K with positive magnetization in the FC curves.

Figures 4a and 4b show the FC χ–T curves measured with several different applied fields between 20 and 10,000 Oe. The paramagnetic susceptibilities above T_N are almost independent of the applied fields. With increasing the field from 20 to 5000 Oe, the absolute values of χ below T_{comp} steadily decrease. Applying the field of 7000 and 10,000 Oe turns the sign of susceptibilities to positive in the whole temperature region. It is also interesting in the figures that all the curves tend to cross around $T_{comp} \sim 163$ K over the whole range of the applied fields.

From the above results, it is obvious that entire alternation of magnetic properties occurs in this solid solution. Though the reversal of magnetization is an unusual phenomenon, it is not entirely without precedent. Similar phenomena have been reported for a few systems such as a perovskite $LaVO_3$ (10–12) and a ferrimagnetic spinel $Co[CoV]O_4$ (13). The compensation temperatures (T_{comp}) are ~ 110–140 K and ~ 70 K for the former and latter systems, respectively. However, to the authors' knowledge, such a distinct diamagnetic effect as that found here has not been reported for the other systems.

The different mechanisms have been proposed for the phenomenon in the above two systems. For $LaVO_3$, it was interpreted in connection with the enhancement of an orbital moment of V, which has an antiparallel coupling with a spin moment (12). The enhancement is brought about by the change of the electronic state of V^{3+} due to a magnetostrictive transition around 138 K, which is slightly lower than a Neel temperature $T_N = 142$ K (12). Though $LaCrO_3$ shows a crystallographic change around 550 K (3), to the authors' knowledge, such a change in perovskite chromates has not been reported around 160–260 K (between T_{comp} and T_N for $La_{0.5}Pr_{0.5}CrO_3$). Thus, at present, the influence of orbital moment as seen in $LaVO_3$ may not be responsible for the present phenomena. The Curie–Weiss fit ($1/\chi = (T - \Theta)/C$) for $La_{0.5}Pr_{0.5}CrO_3$ above ~ 300 K provided the Curie constants (C) almost equal to the contribution of free-ion Pr^{3+} (3.62 μ_B) (14) and spin-only Cr^{3+} ($S = 3/2$; 3.87 μ_B) moments with the nominal molar contents. The Weiss temperatures (Θ) were antiferromagnetic values of ~ -300 K. Thus the $3d$ orbitals of Cr^{3+} are almost quenched above T_N. Crystallographic and electronic structures should be determined below T_N in future.

The results might be understood in terms of different temperature dependence of inequivalent magnetic sublattices as proposed for $Co[CoV]O_4$ where the magnetic Co^{2+} and V^{4+} ions occupy the two different crystallographic sites (12, 13). Apparently there exist such magnetic sublattices of Cr^{3+} and Pr^{3+} in the *Pnma* structure of $La_{0.5}Pr_{0.5}CrO_3$. In perovskites, the directions of exchange fields at the lanthanide sites are usually perpendicular to those of net $3d$ metal moments (15). However, it was proposed for a perovskite chromate $GdCrO_3$ (space group *Pnma*) that the canted-antiferromagnetic order of Cr^{3+} produces an internal field at the Gd^{3+} site, whose direction is opposite to the net Cr^{3+} moment (16). If this situation is assumed for the present system, negative magnetization could be observed at low temperatures where the order of the Pr^{3+} moments is expected to occur.

As is well known, the magnetic order of perovskite oxides is affected also by the ionic radii of lanthanide ions, which govern the magnetic interactions between $3d$ metals via O^{2-} ions. To see this effect, the $La_{1-x}Pr_xCrO_3$ samples have been also prepared with $x = 0.2$, 0.4, 0.6, and 0.8. It is relevant that with increasing x, the lattice parameters changed continuously and the Neel temperature T_N decreased monotonically. It is interesting that all the solid solutions exhibited negative magnetization. In addition, it was found that the absolute values of negative magnetization tended to increase with increasing Pr content (from ~ 20 to ~ 400 emu/mol at 2 K with $H = 100$ Oe), which seems to be consistent with the above speculation. This result cannot be explained in connection only with the change of the Cr–O–Cr angle and indicates the entire alternation of magnetic structures in these solid solutions.

Magnetic structures are obviously to be determined for clarifying the true origin of the behavior. Neutron diffraction measurements will be carried out for this purpose, which reveal also the crystal structures at low temperatures. The studies on magnetic properties also for the other mixed chromates are now in progress, and will be published together with more detailed results on $La_{1-x}Pr_xCrO_3$.

Note added in proof. Magnetization measurements have been done for two $GaCrO_3$ samples with $H = 100$ Oe, showing canted-antiferromagnetism at $T_N \sim 170$ K. Negative magnetization was observed below $T_{comp} \sim 130$ K in FC curves. The maximum absolute value of the negative magnetization (at ~ 25 K) was ~ 30 times as large as that of positive magnetization (at ~ 160 K). This compound also exhibited another T_{comp} of ~ 15 K, below which the sign of magnetization becomes positive. The details will be published in the future.

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