

Unconventional Colossal Magnetoresistance in Sodium Chromium Oxide with a Mixed-Valence State**

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The unusual properties of mixed-valence transition-metal oxides have been challenging the condensed matter community for decades. These include the Verwey transition in iron oxides,^[1] metal-insulator transitions in Magnéli-type titanium and vanadium oxides,^[2] high T_C superconductivity in copper oxides,^[3] and colossal magnetoresistance (CMR) in manganese oxides.^[4] On the other hand, chromium oxides have made little contribution to this important field, mainly because mixed-valence chromium oxides are rare. Cr^{3+} ions in octahedral coordination are very stable owing to the half-occupied t_{2g} states that tend not to coexist with tetravalent chromium ions. Instead of forming a $3d^2$ state, Cr^{4+} donates a hole to the oxygen ligand, thus forming a $3d^3 L$ state with negative charge-transfer energy, as found in CrO_2 for example.^[5] This electronic configuration is expected in any oxide containing Cr^{4+} ions because of the single-ion effect. The recent discovery of potassium chromium hollandite with a unique metal-insulator transition in the ferromagnetic phase suggests that mixed-valence chromium oxides may demonstrate anomalous physical properties related to their unusual electronic states.^[6]

Herein we present calcium ferrite-type NaCr_2O_4 , a new member of the chromium oxide family with mixed-valence $\text{Cr}^{3+}/\text{Cr}^{4+}$ ions. This material demonstrates an unusual CMR effect that is closely related to its unconventional magnetic structure caused by spin frustration. The CMR of this compound is unique from several aspects. First, it is observed in a chromium oxide, not in a manganese oxide. Second, it is found in a single-phase material having an insulating ground state. Third, the CMR is not limited to the vicinity of the magnetic phase transition but becomes progressively more prominent with decreasing temperature down to 0 K. The discovery of the NaCr_2O_4 with a novel CMR mechanism will stimulate further search for new transition-metal CMR compounds other than the manganese oxides. Finding novel

CMR materials is important not only from the viewpoint of fundamental science, but also from the viewpoint of leading technology. The tunnel magnetoresistance (TMR) is a key technology for position sensors, acceleration sensors, and magnetic switches: therefore, the TMR-based devices have been used in a wide variety of machines, including hard disc drives, cameras, computers, mobile phones, cars, and virtual reality systems, including video game consoles and robots. The CMR materials are expected to drastically enhance the performance of these systems by replacing ferromagnetic metal layers in conventional TMR devices.^[7]

NaCr_2O_4 was obtained using a high pressure, high-temperature technique.^[8] It remained highly stable even upon quenching to room temperature. X-ray diffraction studies revealed that NaCr_2O_4 crystallizes in the calcium ferrite type structure ($Pnma$ space group with $a = 9.01873(5)$, $b = 2.913776(15)$, $c = 10.41549(6)$ Å) and is isostructural with $\beta\text{-CaCr}_2\text{O}_4$.^[9] The fit to the diffraction pattern and the structural parameters obtained from Rietveld refinement are shown in Figure 1 and the Supporting Information,

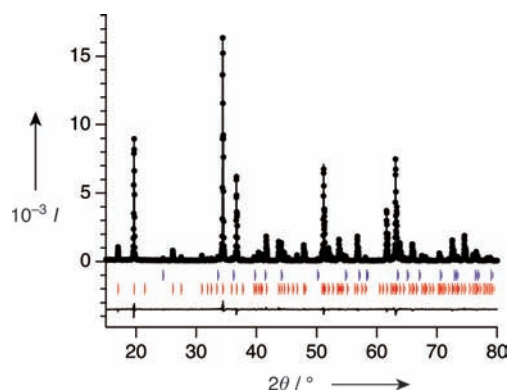


Figure 1. XRD pattern of NaCr_2O_4 . The dots, upper line, and bottom line represent the observed data, calculated pattern, and the difference between them, respectively. The final profile, weighted profile, and goodness of the fit are $R_p = 6.21\%$, $R_{wp} = 8.42\%$, and $S = 1.27$, respectively. All the peaks observed are assigned to NaCr_2O_4 (red vertical bars) or Cr_2O_3 (blue vertical bars). The weight contribution of Cr_2O_3 is approximately 2.0%.

Table S1,^[8] respectively. The crystal structure of NaCr_2O_4 is depicted in Figure 2. The double chains formed by edge-sharing CrO_6 octahedra form important structural units that define the electronic properties of this compound. Both one-dimensional correlation and spin frustration are expected in this structure.

Magnetic susceptibility and magnetization curves are shown in Figure 3a and b, respectively. A magnetic transition

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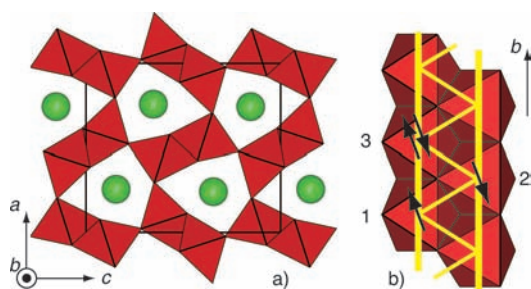


Figure 2. Crystal structure of NaCr_2O_4 . a) Projection onto the ac plane, where the green circles depict Na ions and the octahedra represent CrO_6 units. b) Double-chain unit structure of NaCr_2O_4 . In the double chain, spin frustration may occur at certain conditions. For example, in the case where all the interactions are antiferromagnetic, after the direction of spins 1 and 2 are fixed, the direction of spin 3 cannot be fixed owing to competition between spin 1 and spin 3 and between spin 2 and spin 3.

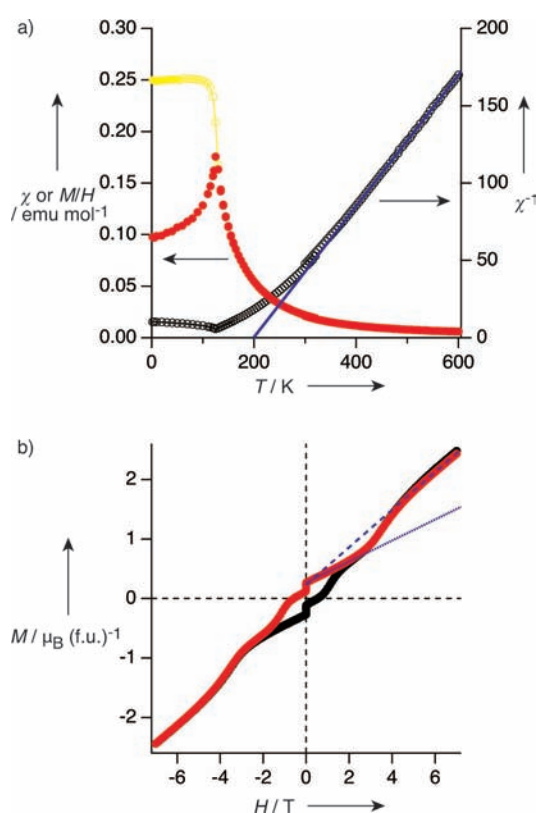


Figure 3. Magnetic properties of NaCr_2O_4 . a) Magnetic susceptibility (red circles) and reciprocal susceptibility (open black circles). The yellow circles represent M/H data at $H = 1$ T. The blue line represents the Curie–Weiss law with $C = 2.36 \text{ emu K mol}^{-1}$ and $\Theta = 199$ K. b) Magnetization curve at 2 K. The red and black circles are data collected with decreasing and increasing fields, respectively. The dotted and broken lines are $M = 0.267 + 0.177H$ and $M = 0.230 + 0.309H$, respectively, which are obtained by a linear fit to the data between 0.1 T and 1 T and between 5 and 7 T, respectively.

is observed at $T_N = 125$ K, below which spontaneous magnetization appears. However, magnetization is far from the saturation value of about $5 \mu_B$, and a spin-flop like transition takes place at a critical field of $H_C = 3.5$ T (Figure 3b). We

conclude, therefore, that the magnetic order in NaCr_2O_4 is antiferromagnetic, not ferromagnetic. It is known that spontaneous magnetization is observed not only in ferromagnetic but also in several antiferromagnetic structures.^[10]

From the magnetization curve between 0.1 and 1 T (Figure 3b), spontaneous magnetization was estimated to be $M_{\text{low}} = 0.267 \mu_B \approx 1/4 \mu_B$. Assuming that Cr^{3+} ($3d^3$) and Cr^{4+} ($3d^2$) have magnetic moments of $3 \mu_B$ and $2 \mu_B$, respectively, there is no possible magnetic structure model with only up- and down-spins that can account for the observed magnetization. Thus, it appears that NaCr_2O_4 has an unconventional magnetic structure, as in the case of $\beta\text{-CaCr}_2\text{O}_4$, the magnetic moments of which rotate cycloidally along the direction of the CrO_6 double chain.^[11] We conjecture that the unconventional magnetic structure in NaCr_2O_4 is caused by spin frustration, as illustrated in Figure 2b for example. From the reciprocal susceptibility data between 450 K and 600 K, the Curie constant and the Weiss temperature were estimated to be $C = 2.36 \text{ emu K mol}^{-1}$ and $\Theta = 199$ K, respectively. The Curie constant is slightly smaller than the theoretical value of $C = 2.88 \text{ emu K mol}^{-1}$,^[12] which may be due to quantum fluctuations enhanced by the low-dimensional spin correlation or spin frustration in the double chains. More importantly, the positive Weiss temperature indicates that the dominant spin interactions are ferromagnetic, although antiferromagnetic interactions are not negligible, as the overall magnetic order in NaCr_2O_4 is antiferromagnetic. These two kinds of interactions cause spin frustration, as shown by the fact that the magnetic transition temperature is significantly lower than the Weiss temperature. Indeed, spin frustration can occur if, for example, the rung interactions (depicted by the thin yellow lines in Figure 2b) in the CrO_6 double chain are ferromagnetic and the leg interactions (the thick yellow lines in Figure 2b) are antiferromagnetic, as found in the case of isostructural NaV_2O_4 .^[13]

The temperature dependence of the electrical resistivity ρ measured at a magnetic field of zero and 9 T is shown in Figure 4a. The zero-field resistivity diverges with decreasing temperature, indicating semiconducting behavior. Indeed, the $\log \rho$ versus $1/T$ plot shows a linear dependence above and below the antiferromagnetic transition temperature $T_N = 125$ K.^[8] From the slope of the $\rho(T)$ dependence, the energy gap was estimated to be $\Delta = 1334$ K for $T > T_N$ and $\Delta = 543$ K for $T < T_N$. On the other hand, the resistivity under a magnetic field of 9 T does not diverge but gradually approaches a finite value at $T \rightarrow 0$ K. As a result, the magnetoresistance (MR), $\text{MR} = \{\rho(H) - \rho(0)\} / \rho(0)$, is close to -100% at low temperatures. It should be noted that the negative CMR in NaCr_2O_4 is closely related to the magnetic structure because it appears only below T_N and because the MR curve at 50 K (Figure 4b) changes slope at around $H_C = 3.2$ T, which is the spin-flop critical field at 50 K.^[8]

In conventional CMR compounds such as manganites, CMR occurs near the ferromagnetic transition temperature because the magnetic field suppresses the thermal fluctuations of parallel spins and, as a result, reduces scattering of charge carriers by the fluctuating spins.^[14] As the thermal fluctuations of spin orientation become smaller at low temperatures, conventional CMR vanishes at temperatures

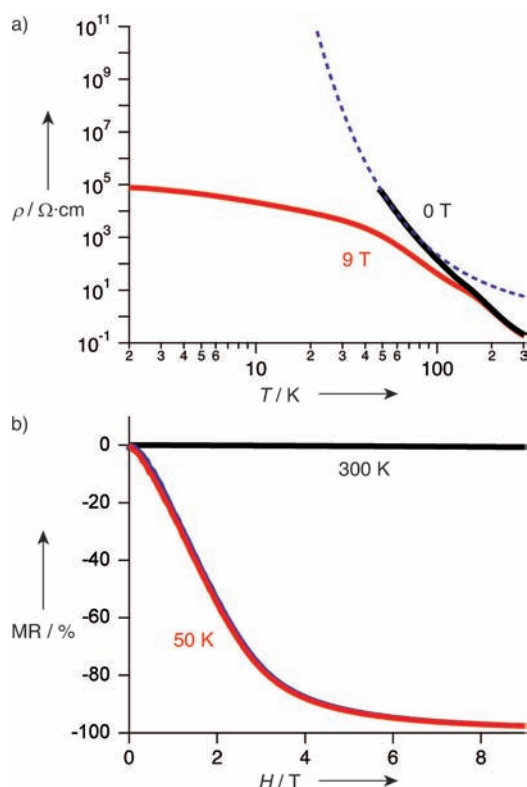


Figure 4. Electrical resistivity of NaCr_2O_4 . a) Temperature dependence under zero field (black line) and 9 T (red line). The broken line represents the calculated curve with an energy gap of $\Delta = 543$ K. b) Magnetic field dependence of MR at 50 K and 300 K. The red and blue lines were measured with decreasing and increasing magnetic fields, respectively. The former almost completely overlaps the latter.

far below the ferromagnetic transition temperature, where the compounds are metallic even without the presence of a magnetic field. In the case of NaCr_2O_4 , this model does not apply at all because NaCr_2O_4 is electrically insulating in the absence of a magnetic field. Therefore, despite the similar magnitude of the MR, one may expect that the mechanism of the CMR effect in NaCr_2O_4 is quite different from that observed in manganites. In fact, the CMR effect in NaCr_2O_4 is not suppressed at lower temperatures but is enhanced.

As for the temperature dependence of CMR in NaCr_2O_4 , it could be argued that there is some phenomenological similarity between the CMR effect in NaCr_2O_4 and that in several manganite solid solutions, such as $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \approx 0.3$) and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x \approx 0.5$).^[15] In other words, the CMR effect in the latter systems is also observed over a wide temperature range below a phase-transition temperature. In these systems, the CMR is caused by competition between ferromagnetic metallic and charge-ordered insulating phases, the relative volumes of which are controlled by the magnetic field.^[16] This electronic phase separation can be identified by the two characteristic features. First, as the charge-ordering transition is accompanied by a structural transition, large thermal and field hysteresis appear in magnetic and transport properties. Second, nearly saturated magnetic moments, at least the moments close to the saturation values of the t_{2g} electrons, appear when the metallic state is stabilized under

a magnetic field. In NaCr_2O_4 , no phase separation was detected by detailed analysis of its structural, magnetic, and thermodynamic properties.^[8] Indeed, NaCr_2O_4 does not show any hysteresis in magnetic and transport measurements, and the magnetization is much smaller than the saturated magnetic moments even at 9 T. These findings support a new mechanism of the CMR effect that is different from that of the manganites.

While the detailed mechanism of the CMR effect is beyond the scope of this current work, it should be pointed out that conical ordering is one of the most probable models of the magnetic structure below 125 K. As spontaneous magnetization can appear from the component of the magnetic moment along the height direction of the cone, the CMR effect can be caused by the increased probability of electron hopping as the aperture of the cone decreases with an increase in the external magnetic field, as shown in Figure 5. Determining the magnetic structure with and without a magnetic field is needed to confirm the proposed mechanism of CMR in NaCr_2O_4 .

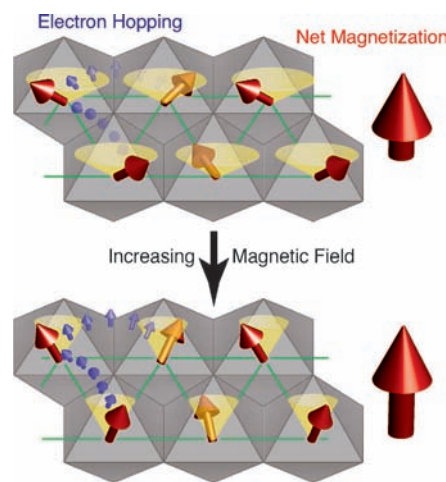


Figure 5. Hypothetical model of the MR effect in NaCr_2O_4 . When the aperture of the cone is large under a low magnetic field, the net magnetization is small and the electron hopping probability is suppressed owing to conservation of spin angular momentum. The external magnetic field reduces the aperture of the cone and increases the probability of electron transfer.

In conclusion, we have discovered calcium ferrite-type NaCr_2O_4 with mixed-valence chromium ions that demonstrates a novel type of CMR effect. We believe that the robust nature of the magnetic structure against an external magnetic field together with a large band gap precludes observation of this type of CMR effect in the vast majority of antiferromagnets. In the case of NaCr_2O_4 , along with the narrow band gap that is due to the unusual electronic state of Cr^{4+} ions, the unconventional magnetic structure formed by spin frustration and one-dimensional correlation is relatively soft. A combination of these factors produces the CMR effect in this compound.

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