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Magnetoresistance of ferromagnetic $Cr_xTi_{1-x}N$ solid solution nitride

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$Cr_xTi_{1-x}N$ solid solution nitrides were prepared by nitridation of Cr-Ti alloys to measure their magnetic and transport properties. The experiment was motivated by calculations on magnetism pointing out similarities of CrN and $LaMnO_3$ (the parent compound of colossal magnetoresistance oxides). The bulk $Cr_{0.5}Ti_{0.5}N$ showed strong ferromagnetism ($T_c \sim 130$ K) while ferromagnetism was very weak for $Cr_{0.67}Ti_{0.33}N$, being consistent with our previous experimental results for epitaxial thin-film samples [Inumaru *et al.*, Appl. Phys. Lett. **91**, 152501 (2007)]. These results confirmed that the ferromagnetism is an intrinsic characteristic of the bulk alloy and cannot be ascribed to lattice strains due to the epitaxy of the films. $Cr_{0.5}Ti_{0.5}N$ showed magnetoresistance of approximately 5% at 5 T. The magnetoresistance was expressed well by a scaling function $-(\rho-\rho_0)/\rho_0 = C(M/M_s)^2$, where M and M_s are the magnetization for a given magnetic field and saturated magnetization, respectively. The constant C for the nitride was 0.14, which was much smaller than that for manganese oxides ($C \sim 4$).

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Transition-metal nitrides are a current field of study in the inorganic synthetic chemistry and physics of condensed matter. Many experimental and theoretical studies that reflect the wide variety of physical properties of transition-metal nitrides have been reported.[1–27] 3*d* transition-metal nitrides show antiferromagnetism (MnN,[1–4] CrN,[5–8] and FeN[9,10]), Pauli paramagnetism (CoN),[11] and superconductivity (TiN and VN).[26] Discovery of the electron-doped layered hafnium nitride superconductor (β-HfNCl) with a T_c as high as 25.5 K (Ref. 27) stimulated interest in the properties of group-IV metal nitrides such as HfN, ZrN, and TiN. Another current topic is the dilute magnetic semiconductor; transition-metal-doped GaN exhibits substantial carrier spin polarization and is attracting much attention.[28–30] $In_{1-x}Cr_xN$ is reported to show ferromagnetism at room temperature.[31] These findings indicate that metal doping is a promising strategy to induce characteristic magnetic and electronic properties of metal nitrides.

Perovskite metal oxides based on $LaMnO_3$ (Refs. 32–34) have attracted much attention owing to the colossal magnetoresistance (CMR) effect. A theoretical study[6] suggested similarity between CrN and $LaMnO_3$; in both, the configurations of magnetic ions are close to $3d^4$ and the Cr-N-Cr interaction in CrN is governed by the double-exchange mechanism to be ferromagnetic (FM). Thus, chemical doping and/or dilution of CrN in a nonmagnetic medium are interesting subjects for experimental study.

Previously, we reported synthesis of epitaxial thin films of $Cr_xTi_{1-x}N$ solid solution with a wide range of x grown by pulsed laser deposition.[35] We found that the material showed ferromagnetism for $x \leq 0.5$. The thin films showed a characteristic dependence of the magnetism on the x values. For $x \leq 0.5$, the films grew coherently on MgO substrates and showed ferromagnetism and magnetoresistance. For $x > 0.5$, the ferromagnetism disappeared and at the same time the lattice of the films relaxed. We could not reveal in our earlier study whether the emergence and disappearance of ferromagnetism was related to lattice strains caused by coherent growth on the substrates. Further study of bulk $Cr_xTi_{1-x}N$ alloy will be needed to clarify this point. The ferromagnetic film showed large magnetoresistance (approximately 7% at 5 T).

Here we report an investigation of a $Cr_xTi_{1-x}N$ powder sample prepared by nitridation of Cr-Ti alloys. We focused on the compounds with $x \sim 0.5-0.8$ because the investigation of the epitaxial films[35] showed a critical change in the ferromagnetism in the x range. Correlation between the magnitude of magnetoresistance and the magnetization was investigated in comparison with the reported CMR manganese oxides.

$Cr_xTi_{1-x}N$ samples (x=0.5, 0.56, and 0.67) were prepared as follows. Granular Cr metal and Ti powder were mixed and pelletized and then melted with an Ar-filled arc furnace. Each sample was melted several times to homogenize the composition. The alloys were then powdered with a diamond file. The obtained powder alloys were nitrided in a quartz tube furnace under deoxygenated nitrogen flow (150 $cm^3 min^{-1}$) at 1273 K for 3.5 h. The magnetizations of the samples were measured with a magnetometer (MPMS-5S, Quantum Design, USA). The electronic conductivity of the samples was measured for a pelletized sample using a four-probe method in the temperature range of 2–250 K. The magnetic field was parallel to the current flow. Powder x-ray diffraction patterns were measured with a Bruker D8 Advance diffractometer (Cu $K\alpha$ radiation).

The nitride samples showed sharp powder x-ray diffraction patterns, which could be indexed on face-centered-cubic unit cells. Figure 1 shows the Cr-content (x) dependence of lattice constants for the $Cr_xTi_{1-x}N$ determined by the x-ray diffraction. The data show that the unit-cell volume monotonically decreased as the Cr content increased. The inset shows magnified plots. The data for the solid solution samples fall on the values close to the solid line, which are drawn using CrN and TiN lattice constants (NaCl type) from the literature. These data indicate that the nitride samples are solid solutions ($Cr_xTi_{1-x}N$) with the NaCl-type structure.

Figure 2 shows typical magnetization behaviors of the samples. The sample with x=0.5 ($Cr_{0.5}Ti_{0.5}N$) had ferromagnetic behavior. Pristine TiN is a metallic (Pauli paramagnetic) compound and Cr ions are believed to bring about the

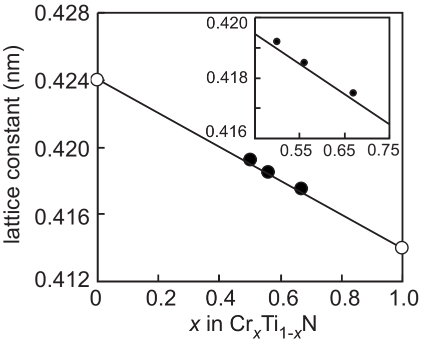

FIG. 1. Lattice constants a as functions of x in $Cr_xTi_{1-x}N$. The solid line is drawn based on CrN and TiN lattice constants reported in the literature. The inset shows the magnified plots.

ferromagnetism. The magnetization was calculated to be 0.62 μ_B per Cr ion. As the Cr content x increased from 0.5, the ferromagnetism steeply decreased as shown in Fig. 2; the ferromagnetism was very weak for $Cr_{0.67}Ti_{0.33}N$. These behaviors are similar to those of epitaxial thin films. The ferromagnetism for the thin-film samples completely disappeared for $x>0.5$. These results confirmed that the ferromagnetism is an intrinsic characteristic of the bulk alloy and cannot be ascribed to the lattice strains due to the epitaxy of the films.

Figure 3 shows the field dependence of magnetization for $Cr_{0.5}Ti_{0.5}N$ measured at different temperatures. At temperatures below 130 K, the sample showed steep increases in magnetization in the low-field region. At 40 K, the magnetization was almost saturated for a field as low as approximately 1000 Oe. The inset shows magnified plots of the data measured at 40 K. Hysteresis with a width of approximately 15 Oe was observed in the magnetization (M) vs the magnetic-field (H) curve. These data confirmed the ferromagnetism of $Cr_{0.5}Ti_{0.5}N$.

Electronic conductivity was measured for pelletized $Cr_{0.5}Ti_{0.5}N$. Figure 4 shows the temperature dependence of resistivity ρ with or without an applied magnetic field. The sample had metallic behavior for the temperature dependence of ρ. The main panel of Fig. 4 compares ρ for the sample at $H=0$ T with that at $H=5$ T. The value of ρ at 0 T steeply decreased when the sample was cooled below T_c (~130 K) while the temperature dependence of ρ above T_c was smaller. The inset in Fig. 4 shows the temperature dependence of the magnetoresistance. The magnetoresistance was observed also at temperatures above T_c (~130 K) to approximately 200 K. As shown in the inset of Fig. 4, the film had maximum magnetoresistance (~5%) at 120 K, which is just below the T_c of the film.

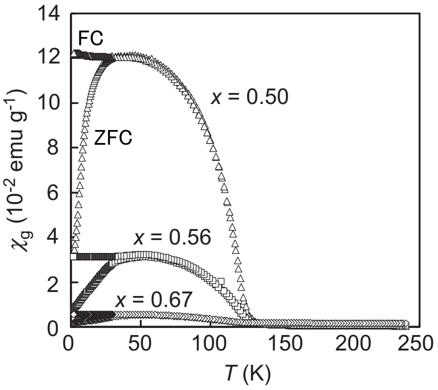

FIG. 2. Magnetization of $Cr_xTi_{1-x}N$ samples as a function of temperature. The magnetic field is 100 Oe.

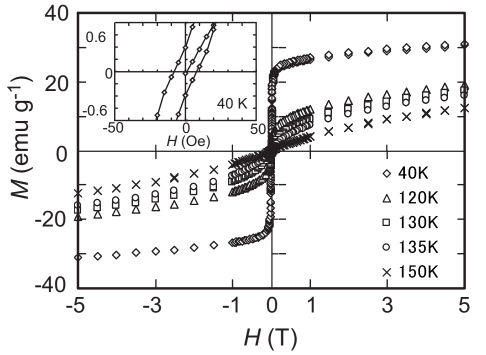

FIG. 3. Field dependence of the magnetization of $Cr_{0.5}Ti_{0.5}N$ at various temperatures. The inset shows the magnified plots.

As we described in a previous communication,[35] it is interesting to discuss the similarity between $LaMnO_3$ and CrN in terms of double-exchange interaction. Filippetti *et al.*[6,7] carried out detailed band calculations for CrN. Competition among spin orderings was discussed with a two-parameter Heisenberg model involving the nearest-neighbor Cr-Cr (J_1) and the next-nearest-neighbor Cr-N-Cr (J_2) interactions. The estimated parameters were $J_1=-9.5$ meV and $J_2=4$ meV. For the Cr-N-Cr interaction, there is a competition between superexchange [antiferromagnetic (AFM)] and double-exchange FM mechanisms involving Cr e_g and N p orbitals and the resulting coupling is FM, owing to the double-exchange interaction as for CMR manganese oxides. Filippetti *et al.* highlighted another similarity between CrN and $LaMnO_3$ in that, for both, the magnetic ions have a equivalent configuration (Cr^{2+} and Mn^{3+}, i.e., $3d^4$) effectively and are octahedrally coordinated by oxygen or nitrogen atoms.

In this study we investigated $Cr_{0.5}Ti_{0.5}N$, which had the strongest ferromagnetism among all $Cr_xTi_{1-x}N$ compounds. The ferromagnetism in this system is considered to be the result of competition between J_1 (AFM direct interaction be-

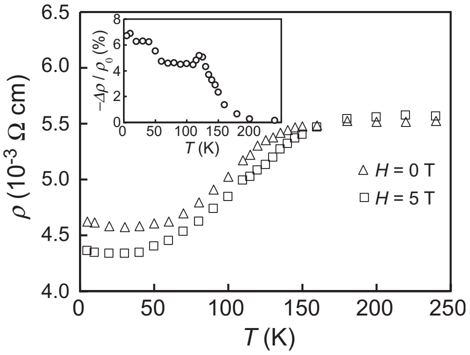

FIG. 4. Temperature dependence of resistivity for $Cr_{0.5}Ti_{0.5}N$ at $H=0$ (triangles) and 5 T (circles). The inset shows the magnitude of the magnetoresistance as a function of temperature.

tween half-filled Cr t_{2g} orbitals) and J_2 (FM interaction governed by the Cr-N-Cr double-exchange mechanism) as discussed by Filippetti *et al.* Considering that ferromagnetism occurred via the formation of the solid solution, the dilution of CrN by TiN may reduce the Cr-Cr neighboring interaction (AFM) to a larger extent than the Cr-N-Cr interaction (FM), although this point should be discussed on the basis of a theoretical quantitative calculation. The important point here is that the origin of the ferromagnetism is the Cr-N-Cr double-exchange interaction. In other words, $Cr_{0.5}Ti_{0.5}N$ is a metal with ferromagnetism governed by the double-exchange interaction similar to the CMR compounds $La_{1-x}Sr_xMnO_3$.

We tried to express the magnitude of the magnetoresistance as a function of the magnetization. In the case of thin films in the previous study, it was difficult to treat the magnetization of the thin films quantitatively because the uncertainty in the film thickness and the interference of diamagnetism from the substrates could not be canceled completely. In the present study, quantitative treatments of the magnetizations were possible. It is well known that magnetoresistance of $La_{1-x}Sr_xMnO_3$ ($x=0.175-0.4$) is well expressed by the scaling function[34]

$$-(\rho-\rho_0)/\rho_0 = C(M/M_s)^2,$$

where M and M_s are the magnetization for a given magnetic field and the saturated magnetization, respectively. Figure 5 shows the correlation between $-(\rho-\rho_0)/\rho_0$ and $(M/M_s)^2$ for the nitride solid solution $Cr_{0.5}Ti_{0.5}N$ at 135 K, which was a temperature slightly higher than the T_c. The magnetoresistance of the nitride was well expressed by the scaling function, suggesting spin-disorder scattering processes. The scaling constant C was 0.13 for the nitride $Cr_{0.5}Ti_{0.5}N$. This value was much smaller than values for the CMR manganese oxides ($C \sim 4$). A theoretical model has quantitatively well described the large C values ($C=1$–4) for the manganese oxides.[36,37] From a structural point of view, a major difference between $Cr_{0.5}Ti_{0.5}N$ and the CMR manganese oxides is that, in CrN, the Cr-N-Cr coupling is smaller than the direct Cr-Cr AFM coupling, whereas for $LaMnO_3$, the Mn-O-Mn coupling is the only relevant interaction. Another important difference is that Cr ions are partially substituted by Ti ions in the case of $Cr_xTi_{1-x}N$ whereas all Mn sites are fully occupied in $La_{1-x}Sr_xMnO_3$. Theoretical studies may be needed for further understanding of the behavior of $Cr_{0.5}Ti_{0.5}N$.

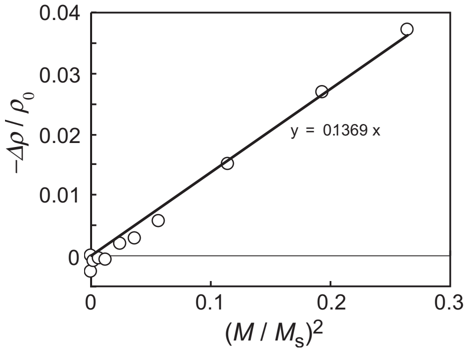

FIG. 5. Magnitude of the magnetoresistance $-(\rho-\rho_0)/\rho_0$ as a function of $C(M/M_s)^2$ for $Cr_{0.5}Ti_{0.5}N$ at 135 K.

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