Magnetic Properties of $(Cr_{1-x}Ni_x)_3Te_4$ with the Pseudo-NiAs-Type Structure

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The magnetic properties of $(Cr_{1-x}Ni_x)_3Te_4$ with the pseudo-NiAs-type structure have been studied. The ferromagnetic transition temperatures for the compounds are found to decrease linearly with the substitution of Ni for Cr, from their magnetization measurements. At low temperatures below 80 K, the magnetization decreases with decreasing temperature; i.e., a weak antiferromagnetic component is superimposed on the ferromagnetism of the $(Cr_{1-x}Ni_x)_3Te_4$ compounds, and the Néel temperature decreases with Ni substitution for Cr. When the magnetization was measured at higher magnetic field or the sample was field-cooled, this antiferromagnetic transition became ambiguous. The experimental results obtained were compared with those for $(Cr_{1-x}Fe_x)_3Te_4$ compounds. © 2000 Academic Press

INTRODUCTION

In the Cr–Te system, ferromagnetic Cr_2Te_3, Cr_3Te_4, Cr_5Te_6, and Cr_7Te_8 are known to exist (1). These compounds have superstructures derivable from the NiAs-type crystal structure, and have metal vacancies (2). According to the phase diagram (3), trigonal Cr_2Te_3 and monoclinic Cr_3Te_4 are stable at room temperature, but at the compositions Cr_5Te_6 and Cr_7Te_8, a two-phase mixture of Cr and Cr_3Te_4 is found.

Among these compounds, we focused on the richest in chromium, Cr_3Te_4. At low temperatures, this Cr_3Te_4 shows the anomaly that magnetization decreases with decreasing temperature; that is, a weak antiferromagnetic component is superimposed on the strong ferromagnetism (4–7). Both the ferromagnetic and antiferromagnetic transition temperatures (T_C, T_N) decrease with increasing chromium vacancy content.

In a previous study (8), the magnetic properties of $(Cr_{1-x}Fe_x)_3Te_4$ with the pseudo-NiAs-type structure have been studied. The effect of the substitution of Fe for Cr on the ferromagnetic and antiferromagnetic transitions for $(Cr_{1-x}Fe_x)_3Te_4$ has been cleared. From both the variation of T_C and the saturation magnetization with Fe content, the solubility limit of the iron-rich side for the hexagonal $(Cr_{1-x}Fe_x)_3Te_4$ with the NiAs-type structure has been estimated.

In the present study, samples of the type $(Cr_{1-x}Ni_x)_3Te_4$ were prepared, in which some nickel atoms substituted for the chromium atoms in the Cr_3Te_4 crystal structure, and their magnetization was measured in the temperature range between 4.2 and 350 K. The objective of this study is to determine how the substitution of nickel for chromium affects the magnetic interaction between the Cr atoms.

EXPERIMENTAL

1. Sample Preparation

The starting materials for all samples were high-purity chromium (99.99%), nickel (99.99%), and tellurium (99.999%). The components were weighed to obtain the desired concentration ($x = 0.01$, 0.02, 0.04, and 0.10 for $(Cr_{1-x}Ni_x)_3Te_4$), intimately mixed, and put into a silica capsule that was then evacuated and finally sealed under vacuum. The sample was heated to 1273 K over a period of 7 days, kept at this temperature for 2 days, annealed at 1073 K for 2 days, and cooled to room temperature. The sample obtained was finely crushed, heated to 1073 K over a period of 2 days, and then tempered for 5 days at 1073 K in another silica–glass ampule. This was slowly cooled to 673 K, kept at this temperature for 10 days, and slowly

cooled to room temperature. The identification of phases and the determination of the lattice parameters of the samples prepared were done by the X-ray diffractometry.

2. Analysis

An X-ray diffraction analysis was performed with $CuK\alpha$ radiation on a RINT 2000 diffractometer (Rigaku) equipped with a curved graphite monochromator. The lattice parameters of the samples were determined by a least-squares method.

3. Magnetic Susceptibility Measurements

The temperature dependence and the field dependence of the magnetization were measured with a commercial SQUID magnetometer (Quantum Design, MPMS 5S model).

The temperature dependence of the magnetization was measured after zero-field cooling (ZFC) and field cooling (FC) processes in the temperature range between 4.5 and 350 K. The external magnetic field applied was 250 G. The field dependence of the magnetization was measured at 10 K by changing the magnetic field strength in the range between $-50,000$ and $50,000$ G.

RESULTS AND DISCUSSION

Cr_3Te_4 crystallizes in the monoclinic Cr_3S_4-type structure. If we draw an ionic picture $Cr^{2+}Cr_2^{3+}Te_4^{2-}$ for Cr_3Te_4, a stable Ni^{2+} ion should be substituted for the Cr^{2+} ion in the $(Cr_{1-x}Ni_x)_3Te_4$ compounds. X-ray diffraction analysis shows that our $(Cr_{1-x}Ni_x)_3Te_4$ compounds with $x = 0.01$, 0.02, and 0.04 have the same crystal structure as the monoclinic Cr_3Te_4. Figure 1 shows the lattice parameters and molar volume of $(Cr_{1-x}Ni_x)_3Te_4$ as a function of Ni content (x). Their lattice parameters decrease with increasing Ni content (x). This is due to the fact that the atomic radius of nickel is smaller than that of chromium (9). In the same figure, the variation of the lattice parameters and molar volume of $(Cr_{1-x}Fe_x)_3Te_4$ with Fe content (x) is also plotted (8). The lattice parameters b and β of $(Cr_{1-x}Ni_x)_3Te_4$ are comparable with those of $(Cr_{1-x}Fe_x)_3Te_4$. On the other hand, the lattice parameters a and c and the molar volume of $(Cr_{1-x}Ni_x)_3Te_4$ are smaller than those of $(Cr_{1-x}Fe_x)_3Te_4$. This is due to the fact that the atomic radius of nickel is smaller than that of iron; i.e., the substitution of Ni for Cr in $(Cr_{1-x}Ni_x)_3Te_4$ is more effective on the size change of the solid solutions than that of Fe for Cr in $(Cr_{1-x}Fe_x)_3Te_4$. The sample with $x = 0.10$ has the NiAs-type crystal structure. Since the crystal structure of Cr_3Te_4 is a deformed NiAs type (Cr_3S_4 type) and its β value is close to $90°$ (2, 10, 11), we will discuss the magnetic properties of $(Cr_{1-x}Ni_x)_3Te_4$ samples having the Cr_3S_4-type crystal structure ($x = 0$–0.04)

and the NiAs-type crystal structure ($x = 0.10$) in the same manner.

From the magnetization and powder neutron diffraction measurements, Cr_3Te_4 has been found to be a ferromagnet below 317–330 K (depending on the exact composition), showing a weak antiferromagnetic component below approximately 80 K (4, 5, 7). These magnetic orders are due to the interaction between Cr atoms. In the $(Cr_{1-x}Ni_x)_3Te_4$ compounds, the magnetic properties should be influenced by the substitution of Ni for Cr. Figure 2 shows the temperature dependence of the magnetization for the $(Cr_{1-x}Ni_x)_3Te_4$ compounds. When the temperature is raised through the ferromagnetic transition temperature, the magnetization of the ferromagnet decreases. The ferromagnetic transition temperature for Cr_3Te_4 has been determined to be 326 K in our previous experiment (8). It is found that the transition temperature T_C for the $(Cr_{1-x}Ni_x)_3Te_4$ compounds decreases with increasing Ni substitution for Cr, due to the magnetic dilution by Ni. Compared with the Curie temperatures for the $(Cr_{1-x}Fe_x)_3Te_4$ compounds, the T_C values for the present $(Cr_{1-x}Ni_x)_3Te_4$ compounds decrease linearly with increasing Ni substitution for Cr up to $x = 0.10$ ($T_C = 293$ K) (see Fig. 4). In the $(Cr_{1-x}Fe_x)_3Te_4$ compounds, the Curie temperatures decrease remarkably with Fe content (x), and the T_C for the sample with $x = 0.10$ is 235 K.

Next we will consider the magnetic properties for $(Cr_{1-x}Ni_x)_3Te_4$ above the Curie temperature, i.e., in the paramagnetic temperature region. As seen in Fig. 2, the magnetization for $(Cr_{1-x}Ni_x)_3Te_4$ decreases with increasing Ni substitution for Cr (x). This is the result of the substitution of Ni for Cr, because the Ni^{2+} ion has a smaller effective magnetic moment than the Cr^{2+} ion. This result is in contrast to the result for $(Cr_{1-x}Fe_x)_3Te_4$, in which the magnetization increases with Fe content (x) (8). In the $(Cr_{1-x}Fe_x)_3Te_4$, a Fe^{3+} ion is substituted for the Cr^{3+} ion and the Fe^{3+} ion has a larger magnetic moment than the Cr^{3+} ion.

At temperatures below 80 K, the magnetization of ferromagnetic Cr_3Te_4 decreases with decreasing temperature. Similar magnetic behavior has been found for the nickel-substituted $(Cr_{1-x}Ni_x)_3Te_4$ compounds (see Fig. 2). Below some temperatures (<80 K), the magnetization decreases with decreasing temperature, which indicates the existence of an antiferromagnetic interaction in these compounds. The Néel temperatures were determined as the temperatures at which the susceptibility decreases maximally with decreasing temperature. With increasing Ni content (x), the antiferromagnetic transition temperature T_N decreases, and the antiferromagnetic interactions become ambiguous in the magnetization vs temperature curve. The sample with $x = 0.10$ shows no antiferromagnetic transition. With increasing applied magnetic field, the antiferromagnetic transition becomes unclear. When the magnetization was
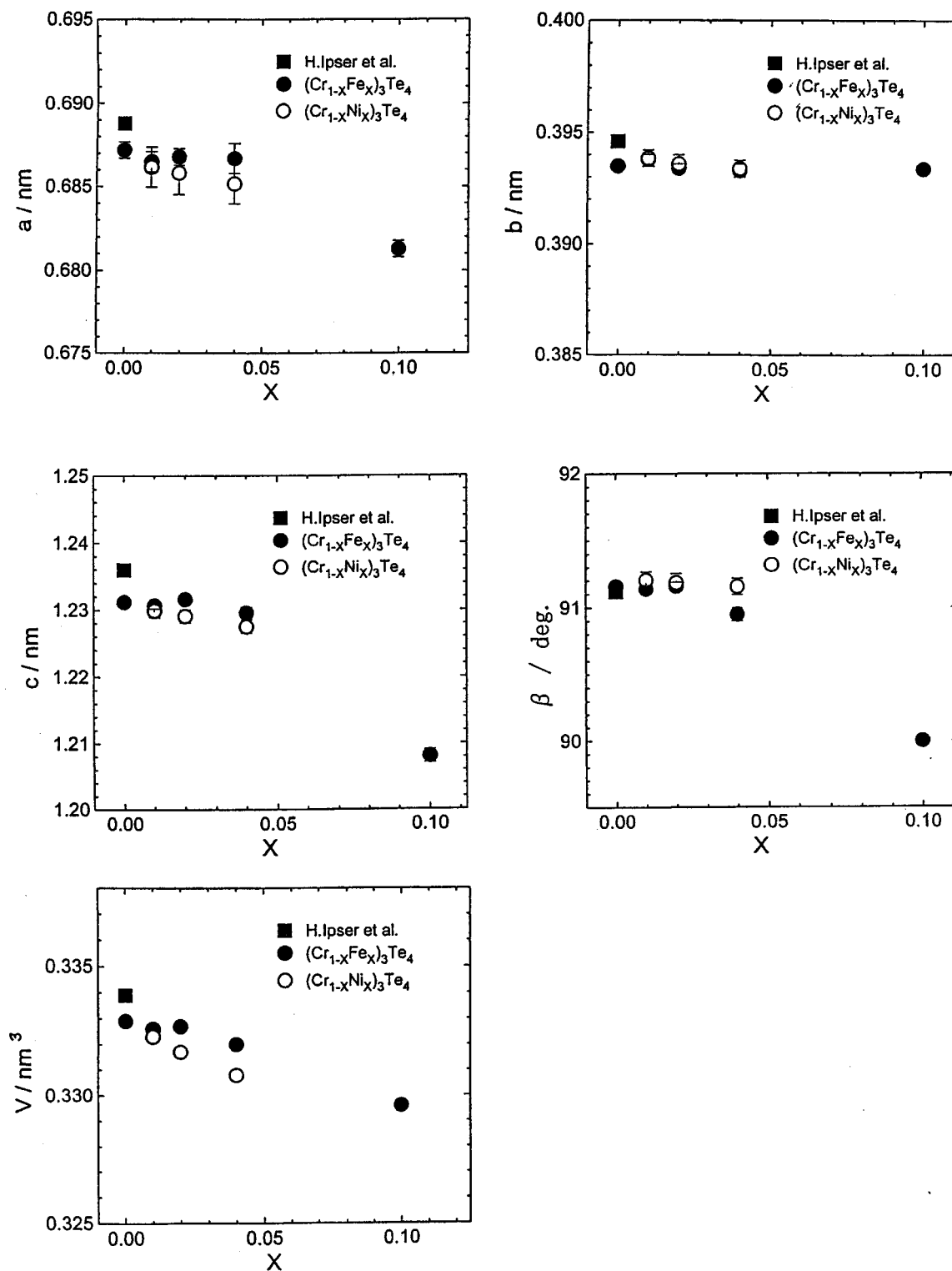
FIG. 1. Lattice parameters and the molar volume of $(Cr_{1-x}Ni_x)_3Te_4$ as a function of Ni content (x). For comparison, those of $(Cr_{1-x}Fe_x)_3Te_4$ as a function of Fe content (x) are also shown.

measured under a field-cooled condition, such an antiferro-magnetic transition has no longer been found. As an example, the temperature dependence of the magnetization for $(Cr_{0.99}Ni_{0.01})_3Te_4$ measured under both the zero-field-cooled condition and the field-cooled condition is shown in Fig. 3.

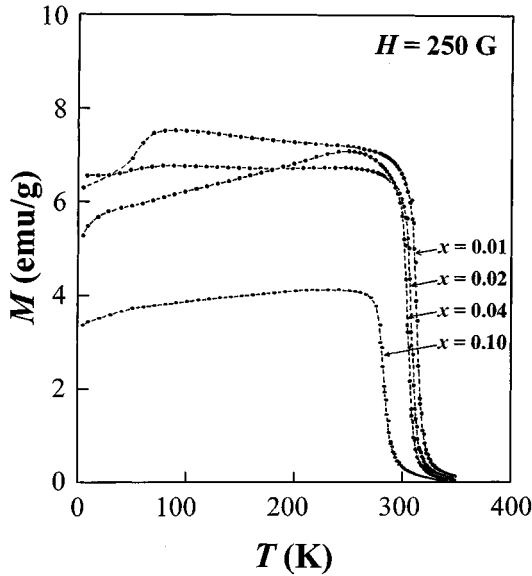FIG. 2. Temperature dependence of magnetization for $(Cr_{1-x}Ni_x)_3Te_4$ in a magnetic field of 250 G.

FIG. 4. Variation of T_C and T_N for $(Cr_{1-x}Ni_x)_3Te_4$ with the x value. For comparison, those for $(Cr_{1-x}Fe_x)_3Te_4$ are also shown. ●,■ for $(Cr_{1-x}Ni_x)_3Te_4$; ○, □ for $(Cr_{1-x}Fe_x)_3Te_4$.

Figure 4 shows the variation of the antiferromagnetic transition temperatures (T_N) and the ferromagnetic transition temperatures (T_C) for the $(Cr_{1-x}Ni_x)_3Te_4$ compounds with the Ni substitution for Cr (x value). The T_N values decrease with increasing Ni content, indicating that the antiferromagnetic transition is due to the interaction between Cr atoms. The available experimental results show
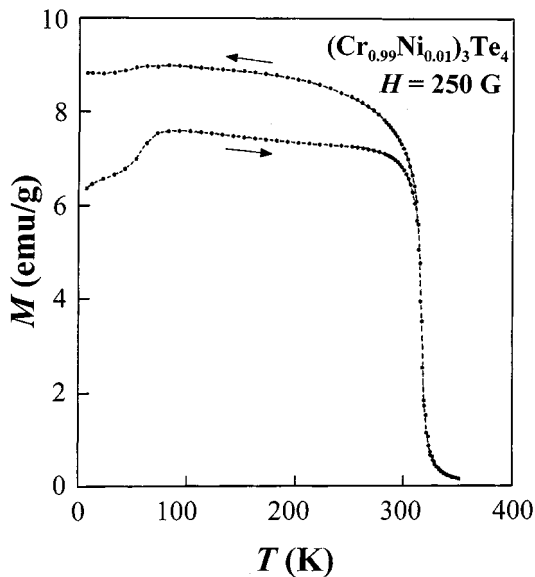

FIG. 3. Temperature dependence of magnetization for $(Cr_{0.99}Ni_{0.01})_3$ Te_4 measured under a zero-field-cooled condition and under a field-cooled condition.

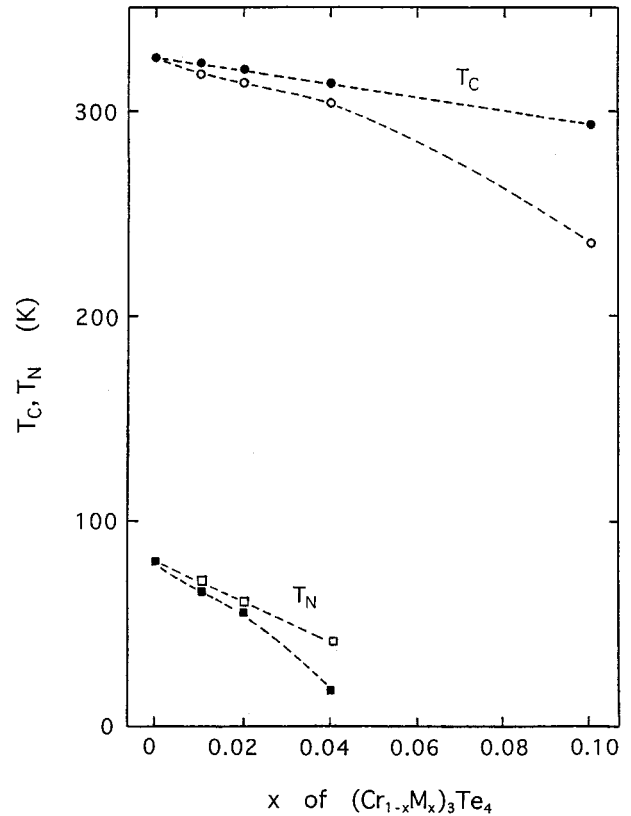that the Néel temperatures decrease almost linearly with increasing Ni content. If this linearity is valid for the $(Cr_{1-x}Ni_x)_3Te_4$ compounds, the Néel temperature for the sample with $x = 0.10$ is estimated to be lower than 4.2 K, which is in agreement with the experimental result that the antiferromagnetic transition is no longer found for $(Cr_{0.90}Ni_{0.10})_3Te_4$. As seen in Fig. 4, both T_C and T_N decrease with increasing Ni substitution for Cr. The decrease of T_N with increasing Ni content is more significant than that of T_C, which indicates that a slight decrease of chromium concentration weakens the antiferromagnetic interaction greatly. This trend accords with the experimental results that the Néel temperature increases in going from Cr_3Te_4 to Cr_5Te_6 to Cr_7Te_8 (7). This is undoubtedly due to the stronger magnetic exchange interaction connected with the filling up of the Cr vacancies.

Figure 5 shows the magnetization curve (magnetization vs applied magnetic field) for $(Cr_{0.99}Ni_{0.01})_3Te_4$ measured at 10 K. The saturation magnetization at 10 K is determined to be 60.85 emu/g. Accordingly, the moment value at saturation is 7.27 μ_B per formula unit. This value is near to a value of 7.62 μ_B derived from neutron diffraction measurements on Cr_3Te_4 (4). In a similar way, the saturation
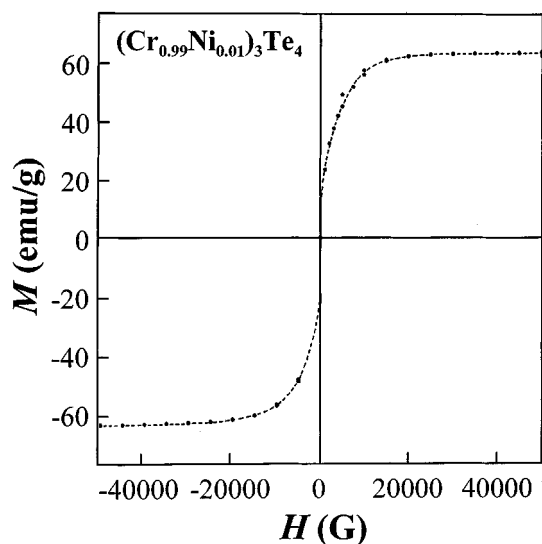
FIG. 5. Field dependence of magnetization for $(Cr_{0.99}Ni_{0.01})_3Te_4$ at 10 K.

magnetization for the samples with $x = 0.02$, 0.04, and 0.10 is obtained to be 59.0, 60.0, and 51.8 emu/g, respectively. With increasing Ni content, the saturation magnetization for the $(Cr_{1-x}Ni_x)_3Te_4$ compounds decreases, which is due to the average decrease of ferromagnetic interactions between metal ions on the substitution of Ni for Cr.

Since Fig. 5 shows the field dependence of magnetization in the range between $-50,000$ and 50,000 G, small hysteresis does not appear. Actually very small magnetic hysteresis exists for $(Cr_{0.99}Ni_{0.01})_3Te_4$ when the magnetization was measured in a lower applied field range ($\sim$250 G), which reflects the divergence of the ZFC and FC magnetic susceptibility at lower temperatures, as shown in Fig. 3.

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