

Magnetic Properties of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$

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The magnetic properties of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with the pseudo-NiAs type structure have been studied. The ferromagnetic transition temperatures (T_C) for the compounds are found to decrease with substitution of Fe for Cr, from the magnetization measurements. From the variation of T_C with x , monoclinic $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x = 0 \sim 0.04$) and hexagonal $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$) are found to be stable at room temperature, and the solubility limit of the iron-rich side for the hexagonal $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ is estimated to be $x = 0.18$. A weak antiferromagnetic transition has been found for monoclinic $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x = 0 \sim 0.04$). The critical Fe concentration (x) at which the antiferromagnetic transition disappears in $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ is estimated to be $x = 0.08$. In the range $x = 0 \sim 0.02$, the saturation magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ increases with x due to the substitution of Fe, which has a larger magnetic moment than Cr. Above $x = 0.04$, the saturation magnetization decreases with increasing x , which is considered to be due to decreased magnetic interaction between metal atoms as a result of the Fe substitution for Cr. From the variation of the saturation magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with x , the solubility limit of the iron-rich side for hexagonal $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ is estimated to be $x = 0.18$. © 1995 Academic Press, Inc.

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. At low temperatures, 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.

Among these compounds, we focused on the richest in chromium, Cr_3Te_4 . Figure 1 shows its crystal structure, determined by Chevreton *et al.* (2). In the figure, Te atoms are omitted. The crystal structure of Cr_3Te_4 is a pseudo-NiAs structure which is distorted to a monoclinic lattice and has the $2c_0$ -type ordering of Cr vacancies. The space group is $I2/m$. Andresen (4) recorded the powder neutron diffraction pattern of Cr_3Te_4 and analyzed its magnetic structure. He found that the ferromagnetic component points along the a -axis, whereas the antiferromagnetic component points along the $(b + c)$ direction. However, Yamaguchi and Hashimoto (7) measured the magnetization of the single crystal of Cr_3Te_4 and found that the easy axis of the saturation moment is parallel to the c -axis in the whole ferromagnetic region and that the antiferromagnetic order appears only in the c -plane.

In this study, samples of the type $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ were prepared, in which some iron substituted for the chromium in the Cr_3Te_4 crystal structure, and their magnetization was measured in the temperature range between 4.2 and 350 K. The main objective of this study is to determine how the substitution of iron for chromium affects the magnetic interaction between the Cr atoms. In addition, the solubility limit of Fe into Cr_3Te_4 was estimated from the change of the magnetic properties of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with Fe content (x value).

EXPERIMENTAL

1. Sample Preparation

The starting materials for all samples were high-purity chromium (99.99%), iron (99.99%), and tellurium

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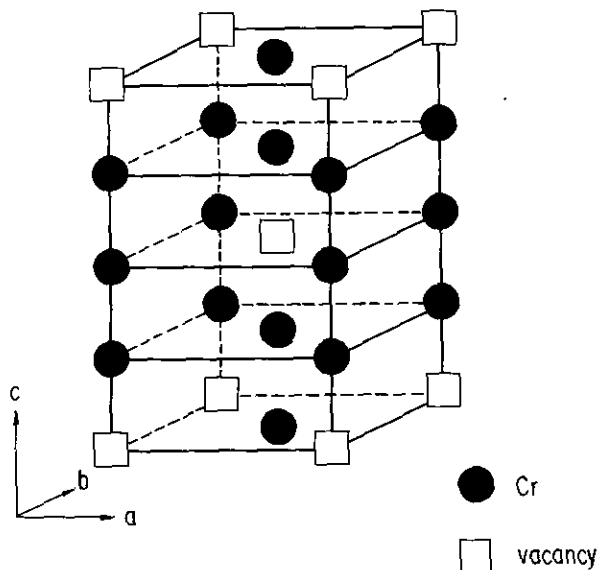


FIG. 1. Unit cell of Cr_3Te_4 . Te atoms are omitted for clarity.

(99.999%). In order to remove superficial oxide by reduction, the iron was heated in purified hydrogen gas, first for 3 hr at 673 K and then for 24 hr at 1273 K. The components were weighed to obtain the desired concentration, intimately mixed, and put into a silica capsule which 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 ampoule. 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 X-ray diffractometry.

2. Magnetization Measurement

The susceptibility and the magnetization were measured both with a Faraday-type torsion balance and with a commercial SQUID magnetometer (Quantum Design, MPMS model). The temperature range of the magnetization measurements with the magnetic balance was between 4.2 K and room temperature. The apparatus was calibrated with $\text{CoHg}(\text{SCN})_4$ as a standard (8). The temperature of the sample was measured by an Ag vs Au-0.07 at. % Fe thermocouple (4.2–40 K) (9) and an Au-Co vs Cu thermocouple (10 K–room temperature). The susceptibility was measured in each of the field strengths of 2800, 4700, 6900, 9000, and 10,600 G. Details of the experimental procedure have been described elsewhere (10). The magnetization measurements with the SQUID magnetometer were car-

ried out at 250 G in the temperature range between 5 and 350 K. To measure the saturation magnetization both at 5 and 150 K for these ferromagnetic samples, the magnetization was also measured in field strengths ranging from 250 to 30,000 G, as indicated in Fig. 6.

RESULTS AND DISCUSSION

Figure 2 shows the lattice parameters and molar volume of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ as a function of Fe content (x). Analysis of X-ray powder diffraction patterns for the Cr_3Te_4 sample showed the existence of a single phase with monoclinic structure. The lattice parameters of monoclinic Cr_3Te_4 prepared in this study are listed in Table 1. They are in good agreement with the data reported by other researchers (see Table 1). The results of the X-ray diffraction measurements (12) show that the samples of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with $x = 0-0.04$ have the same crystal structure as monoclinic Cr_3Te_4 , and that the samples with $x = 0.10$ and 0.15 have the NiAs-type crystal structure (lattice symmetry: hexagonal, space group: $P6_3/mmc$). X-ray diffraction also indicates the sample of $(\text{Cr}_{0.60}\text{Fe}_{0.40})_3\text{Te}_4$ was a mixture of

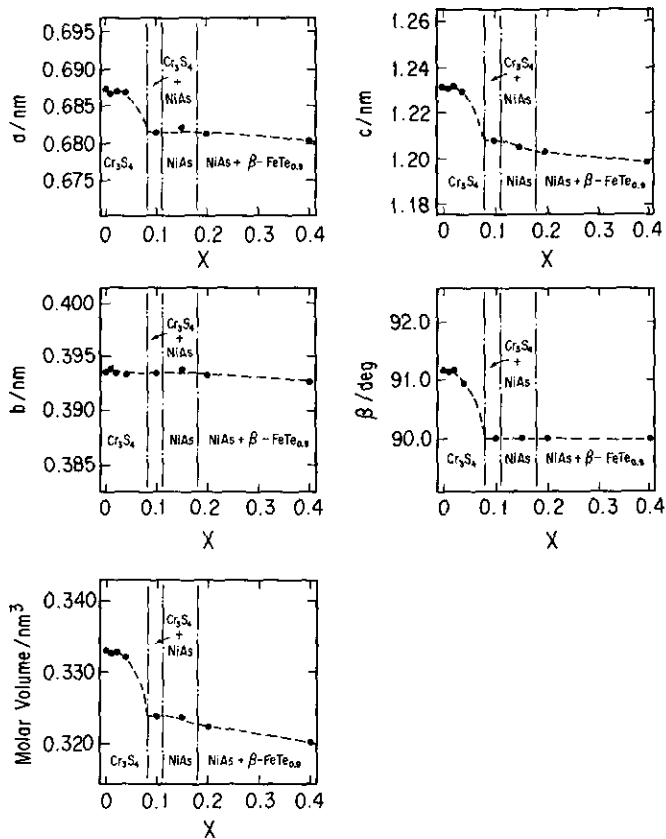


FIG. 2. Lattice parameters and molar volume of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ as a function of Fe content (x). For the NiAs type, the parameters were scaled to correspond to the supercell (see text).

TABLE 1
Lattice Parameters for Cr_3Te_4

| Cr_3Te_4 | Present study | Grønsvold ^a | Ipsier <i>et al.</i> ^b |
|--------------------------|---------------|------------------------|-----------------------------------|
| a (nm) | 0.6872 | 0.6879 | 0.6888 |
| b (nm) | 0.3935 | 0.3934 | 0.3946 |
| c (nm) | 1.2312 | 1.2340 | 1.2360 |
| β (°) | 91.16 | 91.17 | 91.12 |

^a Ref. (11).

^b Ref. (3).

$(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$) with hexagonal crystal structure and $\beta\text{-FeTe}_{0.9}$ with anti-PbO crystal structure, and that the sample of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with $x = 0.20$ was not a single phase of NiAs-type crystal structure. Since the crystal structure of Cr_3Te_4 is a deformed NiAs-type (2) and its β value is close to 90° , the lattice parameters of the NiAs-type (a' and c') can be related to those of Cr_3Te_4 as follows: $a = \sqrt{3}a'$, $b = a'$, $c = 2c'$, and $\beta = 90^\circ$. So, in this study, we will discuss the magnetic properties of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ samples having both Cr_3S_4 -type ($x = 0-0.04$) and NiAs-type ($x \geq 0.10$) crystal structures in the same manner. As seen in Fig. 2, their lattice parameters decrease with increasing Fe content (x) within a single phase. This is due to the fact that the atomic radius of iron is smaller than that of chromium (13).

From the magnetization and powder neutron diffraction measurements, Cr_3Te_4 has been found to be a ferromagnet below 317–330 K (which probably depends on the exact composition) and showing a weak antiferromagnetic component below ca. 80 K (4, 5, 7). These magnetic orders are due to the interaction between Cr atoms. In the $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ compounds, the magnetic properties should be influenced by the substitution of Fe for Cr.

When the temperature is raised through the ferromagnetic transition temperature, the magnetization of the ferromagnet suddenly decreases. This drastic decrease of magnetization is more prominent in the measurements at lower magnetic field. In this work, we have determined the ferromagnetic transition temperature (T_C) for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ compounds through their magnetization measurements in the magnetic field of 250 G. Figure 3 shows the temperature dependence of magnetization per gram of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ measured by SQUID equipment. In Fig. 4, the T_C thus determined is plotted against Fe content (x). The ferromagnetic transition temperature for Cr_3Te_4 is determined to be 326 K. This temperature is quite close to the Curie temperature 325 ± 2 K, which was estimated from the disappearance of the (1 1 0) reflection in the neutron diffraction experiments (4). The T_C transition temperature for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x < 0.10$) decreases greatly with increasing Fe substitution for Cr, due to the magnetic dilution by Fe. For the sample with $x = 0.10$,

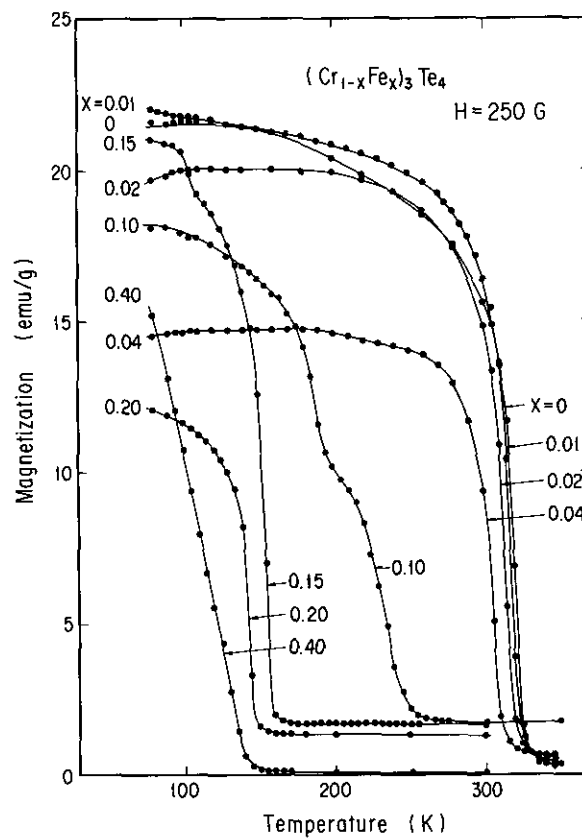


FIG. 3. Temperature dependence of magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ in a magnetic field of 250 G.

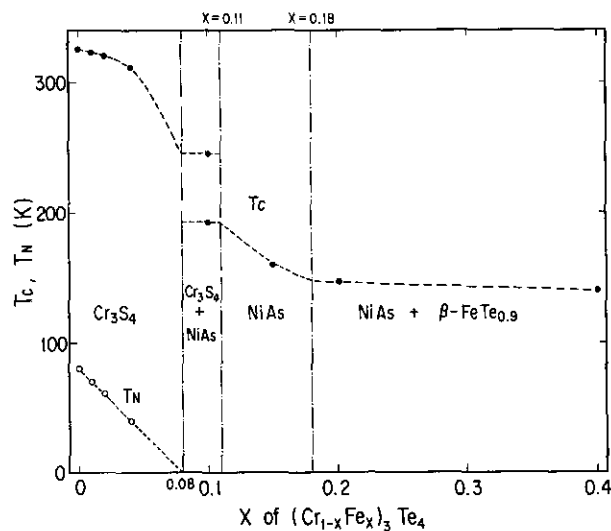


FIG. 4. Variation of magnetic transition temperatures (T_C , T_N) for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with the x value.

two T_C temperatures (193 and 246 K) are seen in Fig. 3, although X-ray diffraction showed only NiAs-type crystal structure. The sample with $x = 0.10$ is considered to be a two-phase mixture of the Cr_3S_4 -type and NiAs-type crystal structures. The solubility limit of the chromium-rich side for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ having NiAs-type structure is estimated to be about $x = 0.11$ from the detection limit of the second phase with the Cr_3S_4 -type structure by X-ray diffractometry. For the sample with $x = 0.15$, the T_C temperature is observed at 160 K, although a small break is seen in Fig. 3. In going from $(\text{Cr}_{0.85}\text{Fe}_{0.15})_3\text{Te}_4$ to $(\text{Cr}_{0.80}\text{Fe}_{0.20})_3\text{Te}_4$, the T_C temperature decreases from 160 K to 147 K, and in going from $(\text{Cr}_{0.80}\text{Fe}_{0.20})_3\text{Te}_4$ to $(\text{Cr}_{0.60}\text{Fe}_{0.40})_3\text{Te}_4$, the T_C temperature decreases only by 7 K. This decrease of T_C with increasing Fe content ($x \geq 0.10$) is considered to be related to the phase relation of Cr_3Te_4 - Fe_3Te_4 . In the single phase region of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$), the T_C temperature can decrease with Fe substitutions for Cr. On the other hand, for $(\text{Cr}_{0.60}\text{Fe}_{0.40})_3\text{Te}_4$, in which the two phases $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$) and $\beta\text{-FeTe}_{0.9}$ coexist, the T_C value is almost the same as for $(\text{Cr}_{0.80}\text{Fe}_{0.20})_3\text{Te}_4$. This behavior of T_C vs x is quite similar to the molar volume change with Fe content seen in Fig. 2 (12). If we assume that T_C for the single phase of $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ decreases with increasing x and that T_C is invariant for the two-phase region, the solubility limit of the iron rich side for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ having the NiAs-type structure is estimated to be about $x = 0.18$.

Here we will consider the magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ above T_C . As shown in Fig. 3, the magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ increases with x ($x < 0.10$), which is the result of the substitution of Fe for Cr, because the Fe^{3+} ion has a larger magnetic moment than the Cr^{3+} ion. It is noticed that the magnetization for the hexagonal-type compound with $x = 0.15$ is higher than that for the monoclinic $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x < 0.10$). We have also tried to obtain the effective magnetic moment. Because the magnetization measurements are limited up to 350 K, the moment obtained was not sufficiently reliable.

It is reported that ferromagnetic Cr_3Te_4 shows a weak antiferromagnetic transition at ca. 80 K (4, 5, 7). Figure 5 shows the temperature dependence of magnetization for the Cr_3Te_4 prepared in this study, which was measured in a magnetic field of 4700 G. Below 80 K, the magnetization decreased with decreasing temperature, which indicates the existence of an antiferromagnetic component in this compound. When the magnetization was measured at higher magnetic field, this transition became ambiguous. The temperature dependence of magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x = 0.01$ and 0.02) is also shown in the same figure. The antiferromagnetic transition temperature decreases with increasing Fe content (x), and the antiferromagnetic interactions become unclear. The compounds, with $x \geq 0.10$ show no antiferromagnetic transition. In Fig.

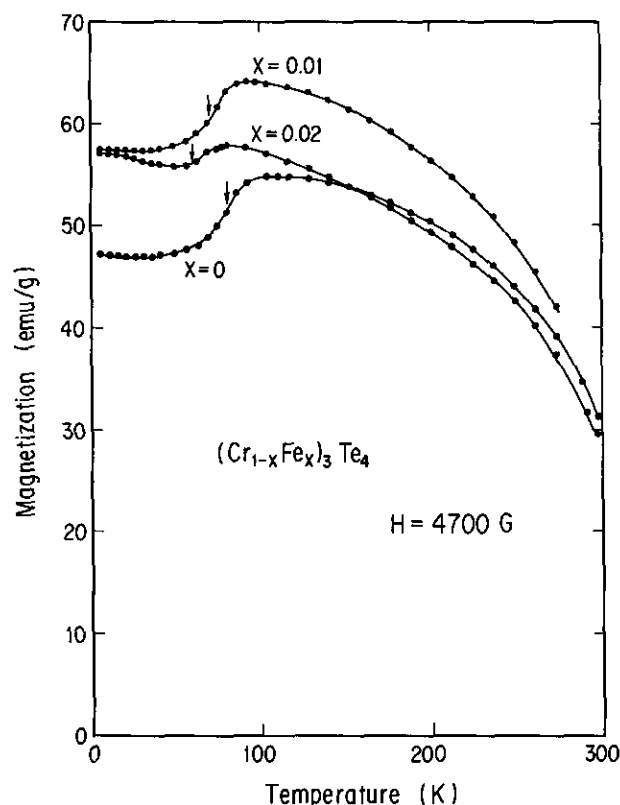


FIG. 5. Temperature dependence of magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x = 0, 0.01$, and 0.02) in a magnetic field of 4700 G.

4, the antiferromagnetic transition temperatures (the Néel temperatures, T_N) for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ are plotted against Fe substitution for Cr (x value). Here, the Néel temperatures were determined as the temperatures at which the susceptibility decreases maximally with decreasing temperature. With increasing Fe content, the T_N value decrease, indicating that the antiferromagnetic transition is due to the interactions between Cr atoms or to their anisotropy. The available experimental results show that the Néel temperatures decrease linearly with increasing Fe content. If this linearity is valid for the $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ compounds with $x \geq 0.10$, their Néel temperatures are 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 compounds with $x \geq 0.10$. The critical Fe concentration (x) at which the antiferromagnetic transition disappears in $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ is estimated from Fig. 4 to be $x = 0.08$. As seen in Fig. 4, both T_C and T_N for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with Cr_3S_4 -type crystal structure decrease with increasing Fe substitution for Cr. However, the decrease of T_N with increasing Fe content is more significant than that of T_C , which indicates that the antiferromagnetism is strongly dependent on the chromium concentration. A slight decrease of chromium concentration weakens the

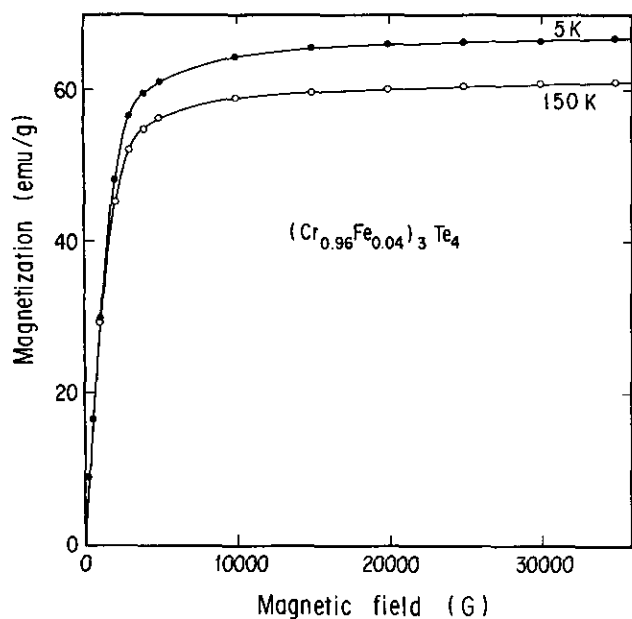


FIG. 6. Field dependence of magnetization for $(\text{Cr}_{0.96}\text{Fe}_{0.04})_3\text{Te}_4$. ●: 5 K, ○: 150 K.

antiferromagnetic interaction greatly, which shows that this antiferromagnetic order can be due to anisotropy of Cr^{2+} .

Next, we will examine the saturation magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$. Figure 6 shows the field dependence of magnetization for $(\text{Cr}_{0.96}\text{Fe}_{0.04})_3\text{Te}_4$. At both 5 and 150 K, the magnetization is found to saturate at a magnetic field of 25,000 G. The saturation magnetizations at 5 and 150 K are 66.9 and 61.0 emu/g, respectively. Figure 7 shows the variation of the saturation magnetization for the $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with Fe content. The saturation magnetiza-

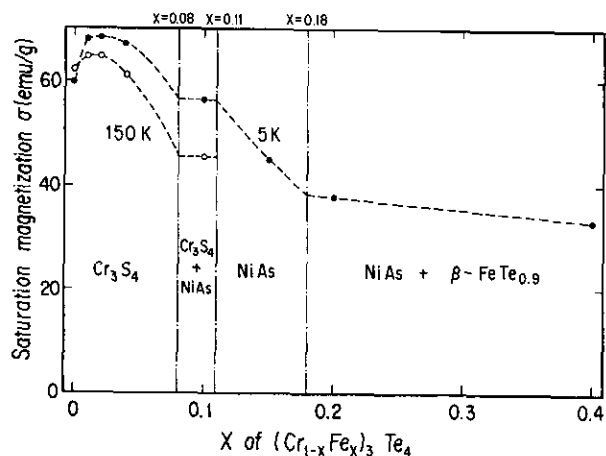


FIG. 7. Variation of saturation magnetization for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with the x value. ●: 5 K, ○: 150 K.

tion for Cr_3Te_4 at 5 K is 59.4 emu/g ($1.77 \mu_B$). This value is consistent with the saturation magnetization of 59.9 ± 0.8 emu/g obtained by Yamaguchi and Hashimoto (7). In going from Cr_3Te_4 to $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x = 0.01$ and 0.02), the saturation magnetization increases with Fe content (x value). This increase is due to the substitution of the Fe^{3+} ion, which has a larger magnetic moment than Cr^{3+} . With further increasing Fe content ($x \geq 0.04$), the saturation magnetization decreases, which is due to the average decrease of ferromagnetic interactions between metal ions on substitution of Fe for Cr. However, the decreases of the saturation magnetization for $(\text{Cr}_{0.80}\text{Fe}_{0.20})_3\text{Te}_4$ and $(\text{Cr}_{0.60}\text{Fe}_{0.40})_3\text{Te}_4$ is not significant. This is due to the fact that two phases exist in these samples. X-ray diffraction analysis shows that $(\text{Cr}_{0.60}\text{Fe}_{0.40})_3\text{Te}_4$ is a mixture of the $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$) phase with NiAs-type structure and the $\beta\text{-FeTe}_{0.9}$ phase with anti-PbO structure. Since the $\beta\text{-FeTe}_{0.9}$ is paramagnetic, its magnetization does not saturate. Therefore, the true value of the saturation magnetization per gram for the sample with $x = 0.40$ should be larger than the experimental value, 32.9 emu/g, but smaller than 44.9 emu/g, the value for $(\text{Cr}_{0.85}\text{Fe}_{0.15})_3\text{Te}_4$, which is a single phase. From both the variation of the T_C temperature for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ (Fig. 4) and the variation of the molar volume with x value (12), the $(\text{Cr}_{0.80}\text{Fe}_{0.20})_3\text{Te}_4$ is also considered a two-phase mixture, which consists of the $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$) phase and the $\beta\text{-FeTe}_{0.9}$ phase. Therefore, the true saturation magnetization per gram for $(\text{Cr}_{0.80}\text{Fe}_{0.20})_3\text{Te}_4$ is also a little larger than the experimental value, 37.7 emu/g. From the variation of the saturation magnetization of the $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with x , the solubility limit of the iron into $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ ($x \sim 0.15$) having NiAs-type structure is estimated to be $x = 0.18$, which is in agreement with the solubility limit estimated from the variation of the T_C temperature for $(\text{Cr}_{1-x}\text{Fe}_x)_3\text{Te}_4$ with the x value.

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