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Study of the Ternary System Fe–Cr–Te Around the Composition $FeCr_2Te_4$

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The system Fe–Cr–Te was investigated around the composition $FeCr_2Te_4$. $FeCr_2Te_4$ is a metastable compound. Single crystals with $Fe_{0.93}Cr_{1.76}Te_4$ composition were grown by vapor transport or the Bridgman method. These crystals are metallic and anisotropic ferromagnets.

1. Introduction

Ternary tellurides and selenides with the general composition $MM_2'Te_4(Se_4)$ (M, M' = transition metal) exhibit a defective NiAs structure (monoclinic I_2/m, Cr_3S_4 type). A large number of these compounds has been reported.

$FeCr_2Te_4$ was first reported by Albers and Rooymans (*1*, *2*). Later, Berodias (*3*), in a general investigation on ternary tellurides got two phases when trying to prepare $FeCr_2Te_4$ by sintering at 1100°C.

The system Fe–Cr–Te was studied around the composition $FeCr_2Te_4$; only defective NiAs structure compounds were prepared. Cr_3Te_4 is a metallic ferromagnet ($T_c \simeq 350°K$). Fe_3Te_4 exhibits a Pauli paramagnetism. The composition of the samples we prepared was assumed to be $\square Fe_xCr_{3-x}Te_4$.

2. Experimental

All the samples corresponding to $\square Fe_xCr_{3-x}Te_4$ were prepared as ingots by direct reaction of high purity elements, according to a method described elsewhere (*4*). The metals were degassed at 1000°C under 10^{-6} Torr; it was necessary to degass the metals, especially chronium, to eliminate adsorbed gases (N_2, CO_2, and O_2). Ingots of different compositions were prepared at 1250°C. (The liquidius line for all compositions is lower than 1250°C). The melted ingots were kept several days at 1250°C, then slowly cooled to a temperature 50°C lower than the liquidius, kept several days at this temperature, and finally either slowly cooled to room temperature or quenched.

3. Results

$FeCr_2Te_4$. This composition can be obtained only as a metastable phase at room temperature by quenching an ingot from 900°C. This composition cristallizes in an NiAs structure: $a = 3.94$; $c = 5.98 \pm 0.01$ Å. No order of vacancies was observed. A second-phase precipitate appears in an ingot of $FeCr_2Te_4$, prepared as described previously, after annealing at 600°C. This precipitate can be seen in microscopic examination (Figs. 1a and 1b). By using an electronic microprobe on the sample shown in Fig. 1b, it was possible to determine the composition of both phases: The composition of the precipitated phase was $FeTe_{0.9}$; the matrix phase was $Fe_{0.5}Cr_{1.8}Te_4$.

These two phases were identified by X rays also; the extra pics correspond to those given

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[*] This paper summarizes the first author's research for his CNAM engineering degree (granted in 1971).

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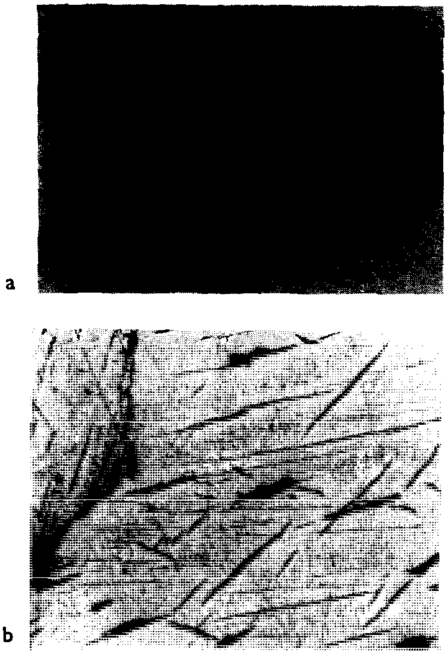

Fig. 1. (a) Micrographic examination in polarized light of a quenched ingot of $FeCr_2Te_4$ after polishing. (b) Micrographic examination of an annealed ingot of $FeCr_2Te_4$ in polarized light. A second-phase precipitate appears at the grain boundaries. (a, ×800; b, ×400).

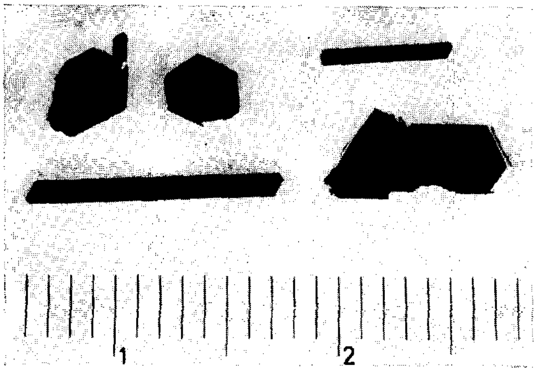

Fig. 2. $Fe_{0.93}Cr_{1.76}Te_4$ crystals from chemical transport. Most of the crystals are platelets perpendicular to the c-axis.

by Grønvold et al. (*5*) for $FeTe_{0.9}$. In conclusion, $FeCr_2Te_4$ does not exist as a stable NiAs phase at room temperature.

Compositions corresponding to $x = 0.25$ and 0.75 were found to be metastable.

Berodias (*3*) also found two phases when trying to get $FeCr_2Te_4$ from powder element at 1100°C: one NiAs phase and $FeTe_{0.8-0.9}$.

4. Crystal Growth–New NiAs Compositions

Chemical transport was used in order to try to grow $FeCr_2Te_4$ crystals. Chemical transport has proven to be suitable for growing ternary compounds or high temperature phase binary compounds, e.g., Fe_2Te_3 (*6*), or even compounds with peritectic decomposition, e.g., $MnTe_2$. [$MnTe_2$, which exhibits a peritectic decomposition, can be grown by chemical transport using iodine (*7*)]. The starting material was a quenched ingot of $FeCr_2Te_4$. Cl_2 was used as a transport agent under the following conditions: $T_2 = 840°C$; $T_1 = 780°C$; and pCl_2 (at $25°C = 0.2$ atm). The crystals we obtained (Fig. 2) look like hexagonal platelets; the c-axis is normal to the plane of the crystals. The chemical composition of the crystals is different from that of $FeCr_2Te_4$, but these crystals are single phase. Wet chemical analysis and electronic microprobe evaluation give $Fe_{0.93}Cr_{1.76}Te_4$. This composition contains more vacancies than $FeCr_2Te_4$, but in the ternary system Fe–Cr–Te it is possible to get a wide range of compositions with NiAs structures having different vacancy concentrations. Chemical transport of binary or ternary compounds with a wide range of composition in a given phase usually provides crystals with a composition different from the source. $Fe_{0.93}Cr_{1.76}Te_4$ (composition of the crystals) and other compositions with the same number of vacancies have been prepared by direct synthesis from the elements. These compositions are stable at room temperature.

$Fe_{0.93}Cr_{1.76}Te_4$ crystallize in a defective NiAs structure: $a = 3.93$, $c = 5.93$Å. Furthermore, it has been possible to grow large single crystals of this composition by the Bridgman method and to take physical measurements.

5. Physical Measurements

The measurements have been carried out on $Fe_{0.93}Cr_{1.76}Te_4$ grown by either transport or the Bridgman method. Results are similar on both kind of crystals.

These compounds are typically metallic $\rho_{77^\circ\mathrm{K}} = 3.3 \times 10^{-4}\,\Omega$ cm.The slope of ρ versus T changes at T_c, as expected in a magnetic metal (*8*). The Hall resistivity ρ_{xy} follows the phenomenological law $\rho_{xy} = R_0 H_Z + R_1 M_Z$ where M_Z = magnetization of the sample; R_1 = spontaneous Hall coefficient; H_Z = applied magnetic field; and R_1 is much greater than R_0 and can only be measured. The transverse magnetoresistance is negative and exhibits a maximum around T_c: –0.008 for 13 kG.

The temperature dependence of the inverse susceptibility is given by $1/\chi = (\mathrm{T} - 155)/3.65)$. The Curie point measured under low-field magnetization is 135°K. The spontaneous magnetization σ_s is 4.40 μ_B per mole.

This material exhibits a strong anisotropy; the *c*-axis is the easy axis. The magnetocristalline anisotropy deduced from magnetization measurements up to 55 kG on single crystals is: $K_{77^\circ\mathrm{K}} = 4.5 \times 10^6$, $K_{20^\circ\mathrm{K}} = 6.0 \times 10^6$, $\mathrm{K}_{4.2^\circ\mathrm{K}} = 6.8 \times 10^6$ erg/cm^3. K_2 is negligible at 20 and 77°K.

Conclusions

Like many of the ternary tellurides, the system Fe–Cr–Te exhibits a wide range of compositions with NiAs structure. $\mathrm{Fe}_{0.93}\mathrm{Cr}_{1.76}\mathrm{Te}$ was grown by either chemical transport or the Bridgman method. These crystals are metallic ferromagnets with a strong uniaxial anisotropy. $\mathrm{FeCr_2Te_4}$ exists only as a metastable phase. Further details on the system Fe–Cr–Te are given in the first author's thesis.

References

1. W. Albers and C. J. H. Rooymans, *Solid State Comm.* **3**, 417 (1965).

2. W. Albers, G. van Aller, and C. Haas, *in* "Colloque Internationale sur les Derivés Semi-métalliques, Orsay, 1965," p. 19, CNRS, Paris (1967).

3. G. Berodias, Thesis, Lyon Univ. (1966).

4. J. P. Suchet and R. Druilhe, in "Colloque Internationale sur les Derivés Semi-métalliques, Orsay, 1965," p. 307, CNRS, Paris (1967).

5. F. Grønvold, N. Haraldsen, and J. Vihonde, *Acta Chem. Scand.* **8**, 1927 (1954).

6. P. Gibart and G. Collin, "Séminaires de Chimie de l'Etat Solide," Vol. 2, p. 127, Masson, Paris (1969).

7. P. Gibart, unpublished results.

8. P. G. de Gennes and J. Friedel, *J. Phys. Chem Solids* **4**, 71 (1958).