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Mössbauer spectroscopy of B8-type Co–Fe–Te and Cr–Fe–Te

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Abstract. The ternary B8-type (NiAs-type) phases in the systems Co–Fe–Te and Cr–Fe–Te have been investigated using Mössbauer spectroscopy in the temperature range 4.2–300 K. Paramagnetic doublets have been observed with linewidths which increase with decreasing temperature. The hyperfine interaction parameters and Debye–Waller factors have been determined. The obvious occurrence of magnetic ordering effects as evidenced by the magnetic susceptibility was found to be reflected as broadening of the Mössbauer resonance lines. The experimentally deduced effective mass implies that the strength of the covalent bonding of the resonant atom to the lattice decreases from Co–Fe–Te to Cr–Fe–Te. This clearly correlates with the increasing ionicity of the chemical bonds as indicated by the systematic changes in the axial ratio c/a and the magnetic moment.

1. Introduction

Owing to a whole number of investigations the magnetic properties of the binary B8-type (NiAs-type) Cr_{1-x}Te , Fe_{1-x}Te and Co_{1-x}Te are well established. Structurally, this particular class of alloys is characterized by a HCP network of Te atoms, the octahedral interstices of the structure being occupied by transition-metal atoms. The deviations from the ideal stoichiometry arise because vacant transition-metal sites give rise to wide ranges of stability and, in many cases, also to the appearance of specifically ordered arrangements of the vacancies. Apart from some not very essential divergences in the interpretation, Co_{1-x}Te ($0.18 \leq x \leq 0.43$) (870 K) shows evidently no tendency of magnetic ordering throughout the range of homogeneity, at least down to 90 K [1]. According to the recent improvements in the phase diagram [2] the total phase field of Cr_{1-x}Te ($0.19 \leq x \leq 0.39$) (870 K) is split into various regions with particular B8-related structures which are well known to be magnetically ordered, some of them even above room temperature [3–6]. In the literature, all Cr tellurides with B8-related structures are considered to be ferromagnetic, although in the special case of Cr_2Te_3 more recent neutron diffraction data seem to point towards a small nearly negligible antiferromagnetic component. The magnetic structure itself is characterized by a collinear arrangement of the magnetic moments along the hexagonal c axis [7]. The inconsistency of the temperature dependence of the magnetic susceptibility in quenched Fe_{1-x}Te ($0.29 \leq x \leq 0.45$) (870 K) alloys compared with that observed directly in the range of the stability of this high-temperature B8 phase seemed to indicate two magnetically different states [8]. The hypothesis of an

antiferromagnetic state formed during the quenching process has never been proved by neutron diffraction and has most probably nothing in common with the hyperfine splitting of the Mössbauer spectrum below 10 K, as reported by Hermon *et al* [9]. Most of the existing Mössbauer data are discussed more in terms of defect ordering and bonding character [10–13].

This rather peculiar magnetic behaviour of Fe_{1-x}Te was the starting point for a number of investigations focused on the systematic changes brought about by the substitution of Fe by other first-row transition metals. Among others, special attention has been paid to the B8-type solid solutions between Fe_{1-x}Te and Co_{1-x}Te at a constant tellurium content of $x = 0.36$, and Fe_{1-x}Te and Cr_{1-x}Te with $x = 0.33$ according to the stoichiometric composition M_2Te_3 .

The marked changes in the magnetic character deduced from the magnetic susceptibility have been reported in two preceding papers [14, 15]. Taking the paramagnetic Curie temperature Θ_p as a measure of the magnetic interactions, the partial substitution of Fe by Cr obviously induced an antiferromagnetic alignment between the neighbouring metal layers normal to the c axis ($\Theta_p < 0$). Increasing amounts of Cr clearly favoured a ferromagnetic coupling between successive metal layers ($\Theta_p > 0$). The substitution of Fe by Co, on the other hand, increased the magnetic susceptibility by nearly one order of magnitude with a maximum located around $y_{\text{Co}}/y_{\text{Fe}} = 1$.

In view of the marked changes signalled by the magnetic susceptibility the application of ^{57}Fe Mössbauer spectroscopy seems to be an appropriate method for promoting the understanding of the observed phenomena.

2. Experimental details

The alloys have been prepared by direct synthesis of the pure elements in evacuated quartz capsules. Iron sheet (Ferrovac E, Vacuum Metals Corporation, Syracuse, NY, USA), chromium lumps (AviQUIPO Corporation, USA), and cobalt sheet (Sherritt Gordon Mines Ltd, Canada) with a nominal purity of 99.99%, and tellurium lumps (Asarco, New York, USA) with a purity of 99.99% were used as starting materials. The pre-reacted ingots were crushed and homogenised under vacuum (0.01 Pa) at suitable temperatures for a period of 2 weeks. FeCoTe_3 (of composition which is not strictly of the given stoichiometry; on account of the phase boundaries the true composition corresponds to 61 at.% Te) was annealed at 870 K, $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ at 1070 K and $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$ at 700 K. After the heat treatment the samples were quenched and identified by x-ray diffraction in 57.3 mm Debye–Scherrer cameras.

Temperature-dependent Mössbauer effect measurements in the range from 4.2 to 300 K were carried out using a constant-acceleration spectrometer in the transmission mode and a liquid-helium cryostat. The temperature control was sufficient to ensure a stability of 1 K for the time necessary to accumulate the Mössbauer data at each temperature point. The spectrometer was calibrated using metallic iron foil and the data reduction was effected using the non-linear least-squares fitting subroutine.

3. Results and discussion

The alloys used for the Mössbauer spectroscopy measurements were selected so as to represent certain composition ranges distinguished by individual magnetic properties: $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ was representative of the iron-rich Cr–Fe–Te alloys with presumably antiferromagnetic interactions along the c axis of the hexagonal B8 structure,

$\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$ representative of the chromium-rich range characterized by ferromagnetic interactions, and CoFeTe_3 representative of the alloys with an anomalously increased paramagnetism compared with the binary alloys Co_{1-x}Te and Fe_{1-x}Te . The observed resonance effect was small owing to the high non-resonant scattering cross section which necessitated long running times per temperature point. Paramagnetic spectra were observed which were fitted with a doublet assuming that iron atoms occupy approximately the same crystallographic site. In view of the non-uniform distribution of the metal vacancies in the binary alloys—especially in the case of the chromium tellurides where numerous types of superstructures are reported [2]. This assumption seems not to be strictly realistic; however, owing to the unknown distribution in the ternary alloys it was difficult to assign unambiguously more than one crystallographic site. A linewidth of resonant line at room temperature of 0.32 mm s^{-1} or less supports this assumption. In table 1 the isomer shifts refer to the fitted data of CoFeTe_3 and $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ at 80 K and $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$ at 130 K while the quadrupole-splitting values are those measured at room temperature. As apparent from measurements in the temperature range from 300 K down to 80 K, the width of the resonance line of CoFeTe_3 and $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ shows a slight increase with decreasing temperature, whereas a more pronounced increase was observed in $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$. Subsequent measurements at 4.2 K have shown much broadened absorption doublets for the three samples (figure 1).

Table 1. Hyperfine interaction and lattice dynamical data.

	FeCoTe_3	$\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$	$\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$
Isomer shift (mm s^{-1})	0.60(2) ^a	0.76(2) ^a	0.80(4) ^b
Quadrupole splitting (mm s^{-1})	0.25(2) ^c	0.29(2) ^c	0.32(2) ^c
dis/dT ($10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$)	3.14(70)	4.64(130)	5.32(80)
M_{eff} (g mol^{-1})	132(30)	90(25)	78(12)
$d\{\ln[A(T)/A(80)]\}/dT$ ($10^{-3} \text{ mm s}^{-1} \text{ K}^{-1}$)	1.51(8)	1.88(8)	2.84(16)
Θ_M (K)	300(16)	263(11)	219(12)
f at 295 K	0.64(3)	0.56(3)	0.43(4)

^a At 80 K.

^b At 130 K.

^c At 300 K.

The linewidth, or the full width at half-maximum, and the shape of the Mössbauer absorption line can provide information about the dynamics of electronic relaxations and in many cases it is an indication of partially resolved hyperfine interactions. One may suggest that the line broadening in these alloys is due to some kind of magnetic ordering as indicated by the magnetic susceptibility data. Obviously, we are faced with competing interactions, where the electric and magnetic interactions are comparable. In addition, the noticeably low resolution makes it difficult to resolve the individual components of the magnetic hyperfine spectrum. We have thus taken the total width of the Mössbauer resonance peak as a qualitative estimate of the magnetic ordering. Figure 2 illustrates the progressive variation in the total linewidth with temperature. The slight increase in linewidth with decreasing temperature in CoFeTe_3 and $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ in the temperature range 300–80 K may be correlated with results obtained from earlier magnetic susceptibility and magnetization measurements. For CoFeTe_3 the change in magnetic susceptibility by about an order of magnitude occurs very smoothly within an extremely wide temperature interval 100–1100 K [14].

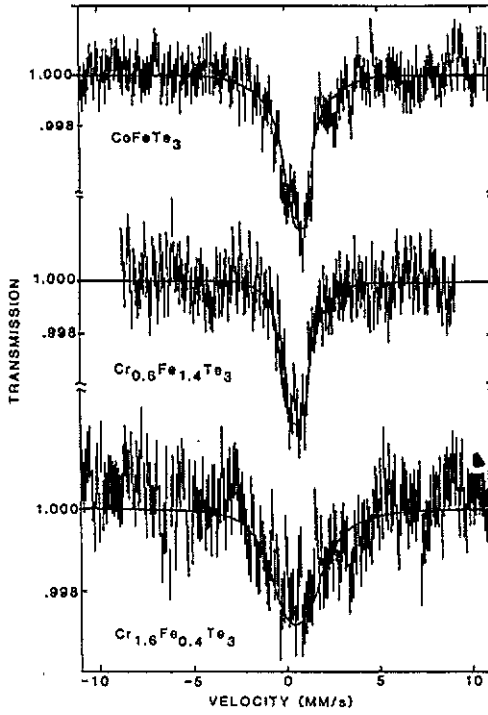


Figure 1. Mössbauer spectra of the samples at 4.2 K.

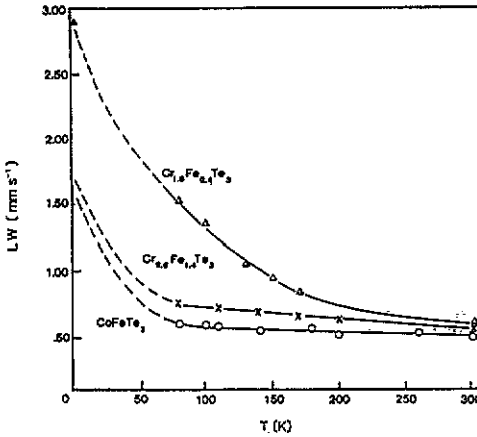


Figure 2. Temperature dependence of the total linewidth LW of the resonance line.

Similarly, magnetization data for $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ resulting in non-zero magnetization (2 emu g^{-1} at 80 K) clearly points towards a magnetically ordered state. In both alloys the transition is not very pronounced down to 80 K. However, measurements at liquid-helium temperature show that the total linewidths for both systems increase by about three times their value at 80 K: 1.6 mm s^{-1} for CoFeTe_3 and 1.7 mm s^{-1} for $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$. This sharp increase in the linewidth at 4.2 K suggests that the transition temperature may be well above this temperature. By contrast, in $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$ the significant increase in linewidth below 200 K clearly coincides with the onset of magnetic ordering and supports the magnetization data which suggests that the ordering starts about 170 K [15]. Because of the unresolved hyperfine spectra it was impossible to deduce more details about these interesting magnetic transitions. On the other hand, the Debye-Waller factor f and its temperature dependence provide information about the lattice dynamical properties of the solid state which are associated with the motion of the Mössbauer atom. The isomer shift and the quadrupole splitting in these materials are characteristics of high-spin Fe^{3+} covalently bonded to the lattice. Both the isomer shift and the quadrupole splitting increase gradually from FeCoTe_3 to $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$ (table 1). Considering the isomer shift which basically accounts for changes in the s-electron density as a guiding factor, the degree of covalency decreases in the same order.

The temperature dependence of the recoil-free fraction for the ^{57}Fe Mössbauer transition can be extracted from the temperature dependence of the area under the resonance curve, and such data are shown in figure 3(a). Using the Debye model in the high-temperature limit ($T > \Theta_M/2$), a lattice temperature Θ_M may be calculated from the temperature dependence of the area under the resonance curve [16]. The f -factors at room temperature (295 K) were then estimated and presented in table 1. The differences in the f -factors of the alloys reflect the variation in the phonon spectra around the Mössbauer atom. Moreover, the data also suggest a stronger covalent character of the structure in FeCoTe_3 than in $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$ or $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$.

The strength of the interatomic bonding forces of the probe atom to the lattice may be provided from a phenomenological effective mass M_{eff} which gives a qualitative estimate of the chemical bonding of the resonant atom to the lattice. M_{eff} can be calculated from the temperature dependence dis/dT of the isomer shift for $T > \Theta_M/2$ from the relationship [16]

$$\text{dis}/dT = -3E_\gamma k_B / M_{\text{eff}} c^2 \quad (1)$$

where E_γ is the Mössbauer transition energy, c is the velocity of light and k_B is the Boltzmann constant. The temperature dependence of the isomer shift of the three samples are shown in figure 3(b) and the respective effective masses are listed in table 1. These give an M_{eff} of 132 g mol^{-1} for CoFeTe_3 , 90 g mol^{-1} for $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$, and 78 g mol^{-1} for $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$. The higher effective mass implies that the bonding interaction force between the Mössbauer atom and its neighbours is stronger in CoFeTe_3 than in $\text{Cr}_{0.6}\text{Fe}_{1.4}\text{Te}_3$, or in $\text{Cr}_{1.6}\text{Fe}_{0.4}\text{Te}_3$.

Such arguments concerning the differences in chemical bond character are strongly supported by the magnetic and the crystallographic data which give some hints at the ionic contribution to the chemical bond. Although most of the phases with the B8-related structures appear to be metallic—a fact which is most commonly ascribed to metallic bonds between neighbouring transition-metal atoms along the c axis—at least a partial ionic character variable from compound to compound seems to be

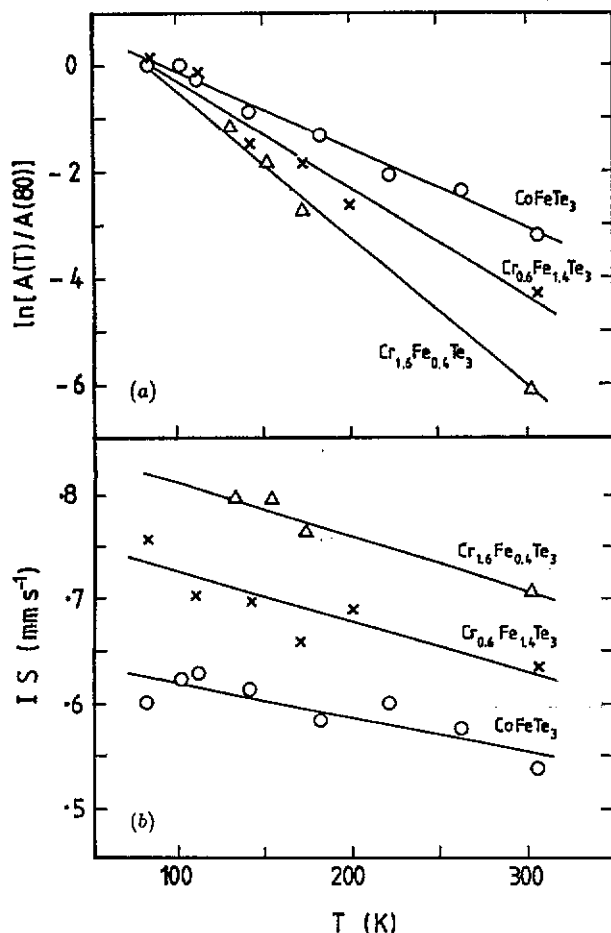


Figure 3. (a) Temperature dependence of the area under the resonance curve; (b) temperature dependence of the isomer shift IS . The full lines are linear regression fits to the data.

indicated. Owing to the contraction of the hexagonal unit cell along the c axis caused by the metallic bonding between the transition-metal atoms the axial ratio c/a is reduced from its ideal value of 1.63. Thus the axial ratio can be taken as a rough estimate for the ionicity of the chemical bonds and, in fact, most of the B8 phases show considerably reduced axial ratios as a result of their metallic character. To the same extent the magnetic moments are expected to be reduced compared with the ionic values which are determined by the electronic configuration of the ionic cores. Applied to the present case we would expect the transition-metal atoms in a trivalent state with an electronic high-spin configuration. This assumption takes account of the stoichiometry M_2T_3 and furthermore seems to be in accordance with the magnitude of the isomer shift and the quadrupole splitting. Accordingly, the effective magnetic moments were assumed to be $3.87\mu_B$ for Cr^{3+} , $5.92\mu_B$ for Fe^{3+} and $4.90\mu_B$ for Co^{3+} (μ_B is the Bohr magneton).

The dimensions of the unit cell are given in table 2, together with the axial ratio c/a and the factor $1 - (c/a)/(c/a)_{id}$ which stands for the reduction in c/a from the

Table 2. Lattice parameters and effective magnetic moments.

	FeCoTe ₃	Cr _{0.6} Fe _{1.4} Te ₃	Cr _{1.6} Fe _{0.4} Te ₃
<i>a</i> (nm)	0.3853	0.3868	0.3926
<i>c</i> (nm)	0.5458	0.5773	0.5988
<i>c/a</i>	1.417	1.493	1.525
$1 - (c/a)/(c/a)_{id}$	0.131	0.084	0.064
m_{obs} (μB)	<1	4.34	4.14
m_{ion} (μB)	5.41	5.30	4.28
$1 - m_{obs}/m_{ion}$	>0.8	0.181	0.033

ideal ionic value $(c/a)_{id}$. The experimentally observed effective magnetic moments m_{obs} , the average ionic moments m_{ion} per atom calculated assuming additive Curie constants, and the factor $1 - m_{obs}/M_{ion}$ as measured for the reduction in the magnetic moments from their ionic values are also included. It is apparent (table 2) that the axial ratios—although larger than the typical metallic value of 1.25—clearly increase in the order FeCoTe₃ → Cr_{0.6}Fe_{1.4}Te₃ → Cr_{1.6}Fe_{0.4}Te₃; however, even for Cr_{1.6}Fe_{0.4}Te₃ it is still smaller than 1.63 which is the value for ideal ionic packing. Similarly, the observed magnetic moments are also smaller than those calculated for a corresponding mixture of free ions. The reduction factor decreases in the same sense as that of the axial ratio which clearly points towards a partial ionic character increasing from FeCoTe₃ to Cr_{1.6}Fe_{0.4}Te₃.

Obviously, these trends substantiate the conclusions drawn from the isomer shift, the quadrupole splitting, the recoil-free fraction and the effective mass which all suggest that the strength of the covalent bonding of the resonant atoms to the lattice decreases gradually from FeCoTe₃ to Cr_{1.6}Fe_{0.4}Te₃. The interpretation of the B8-related structures in terms of an interplay of ionic and metallic bonds is doubtlessly more hypothetical than realistic and there is no reason to exclude the existence of covalent bonds. The experimental methods applied in this paper are certainly not adequate to answer ultimately the question of chemical bonding; however, it seems that, at least in the materials considered in this paper, decreasing covalency as indicated by the Mössbauer data has the same meaning as increasing ionic character as apparent from the lattice parameters and the magnetic data.

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