JOURNAL OF MATERIALS SCIENCE 23 (1988) 3490–3494

Magnetic properties of $(Fe_{1-x}M_x)_7Se_8$

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The temperature dependence of the magnetization of the quenched and slowly cooled samples of Fe_7Se_8 and $(Fe_{1-x}M_x)_7Se_8$ samples with M = cobalt and nickel and x = 0.02, 0.05 and 0.08 are given. All the thermomagnetic curves obtained belong to the Weiss ferrimagnetic type. Discontinuities indicating a magnetic transformation to antiferromagnetic order were obtained for some samples. The magnetic moment at 0 and 78 K (M_0 and M_{78}) dependence on nickel and cobalt concentrations are given. The temperature dependence of the reciprocal susceptibility in the paramagnetic range was studied, and the asymptotic Curie points are given. The values of the effective magnetic moment, μ_{eff}, and the number of unpaired electrons were calculated. The thermal variation of the electrical conductivity of the host material, Fe_7Se_8, is given.

1. Introduction

The magnetic properties of the compounds formed between the various elements of the chalcogen group and the element of iron group are complicated. This was attributed to the various possible distributions of the magnetic moments of cations (Fe) in the crystal [1, 2]. It follows that a different magnetic coupling will occur by replacing cations by another kind of atom of the same chemical group. The formation of phases with metal deficient NiAs-type structure is common to the binary systems of 3d-transition metals with the heavier chalcogen elements [2]. NiSe is weakly paramagnetic [3]. CoSe shows a Curie–Weiss type magnetism [4]. Iron selenides exhibit both antiferromagnetic and ferrimagnetic behaviour depending on composition and temperature [5, 6]. Fe_7S_8 is the most highly magnetic and the most highly conducting for electricity of all other iron sulphides [7, 8]. Why there are different types of magnetism in these alloys is not fully understood. The fact that the nature of the conduction carriers in the semiconducting compounds containing transition elements in most cases is not fully clear [9–11] and the expected similarity between the ferrimagnetism of FeS_x and that of $FeSe_x$ encouraged us to study the magnetic properties of the Fe_7Se_8 system when some iron atoms are replaced by cobalt and nickel atoms.

2. Experimental procedure

The samples were prepared by direct alloying of pure iron powder, 99.90%, and selenium granules, 99.999%. Iron was partially replaced by nickel powder, 99.90%, and cobalt, 99.90%, in appropriate amounts. The mixture was heated in evacuated silica tubes at a temperature of ~1300 K for 70 h and then it was quenched to room temperature. To obtain the same crystal structure for all samples, and based upon the phase diagram for the system $FeSe_x$ given by Serre and Druile [12], the quenched specimens were ground and once more homogenized at 1100 K for 14 days in evacuated silica tubes. Group I of the samples was cooled rapidly, while group II was cooled slowly at a rate of $2\,K\,min^{-1}$. X-ray diffraction patterns were taken using Cu$K\alpha$ radiation with a nickel filter. All the samples have the hexagonal NiAs-type structure [13].

The d.c. resistivity was measured in the temperature range 130 to 600 K. The temperature was increased in steps of 5 K and the measurements were recorded 5 min after the required temperature had been reached. No hysteresis was noticed on heating–cooling runs.

A Gouy-type magnetic balance was used for measuring the magnetic properties. The weights of the specimens used were several milligrams for the measurement in the ferrimagnetic region and several hundred milligrams for the paramagnetic region. The measurements were carried out in the temperature range 78 to 1000 K in a magnetic field of 3 kOe. The saturation magnetizations were obtained by extrapolating the magnetization–magnetic field dependence for zero field at liquid nitrogen temperature. The effective magnetic moments were derived from the reciprocal susceptibility–temperature relation ($1/\chi - T$) in the paramagnetic linear part

$$\chi = \frac{C}{T - \theta_p}$$

where θ_p is the asymptotic Curie temperature and C is the Curie constant.

3. Results and discussion

3.1. The ferrimagnetic region

The temperature dependence of the magnetization of the quenched and slowly cooled samples of Fe_7Se_8 and $(Fe_{1-x}M_x)_7Se_8$ samples (M is the transition metal cobalt or nickel and x = 0.02, 0.05 and 0.08) is shown in Figs 1 and 2. Previous experiments [5] had shown that the magnetic behaviour of Fe–Se depends on the thermal treatment. Thus, it has become essential to compare results on samples quenched from about 1000 K (Fig. 1) with those obtained on slowly cooled

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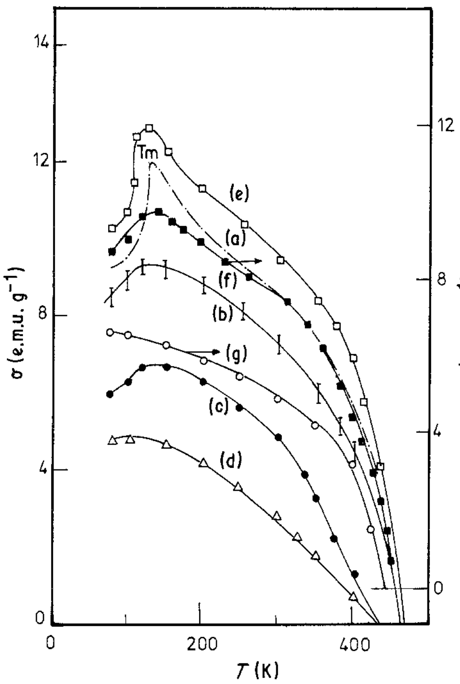

Figure 1 Magnetization–temperature dependence for quenched $(Fe_{1-x}M_x)_7Se_8$ samples. Left-hand axis: (a) $x = 0$, (b) M = Ni, $x = 0.02$, (c) M = Ni, $x = 0.05$, (d) M = Ni, $x = 0.08$, (e) M = Co, $x = 0.02$. Right-hand axis: (f) Co, $x = 0.05$, (g) M = Co, $x = 0.08$.

samples at a rate of $2\,K\,min^{-1}$ (Fig. 2). For the host sample (Fe_7Se_8), no difference between results was obtained (Fig. 1).

The magnetization–temperature curves for all alloys under investigation belong to the Weiss ferrimagnetic type with the ferrimagnetic Curie temperature, T_c, around 445 K. An increase of cobalt or nickel decreases T_c. However, the smallest value of T_c was obtained for the slowly cooled sample which contained cobalt with $x = 0.08$ ($T_c = 420\,K$).

For all alloys under investigation, discontinuities were found at low temperature, T_m, indicating a magnetic transformation to antiferromagnetic order similar to that found in the host material Fe_7Se_8 (Fig. 1). The replacement of iron by cobalt or nickel with $x = 0.02$ and 0.05 slightly shifts the transition towards lower temperatures. This means that these contents of cobalt and nickel slightly stabilized the ferrimagnetic at the expense of the antiferromagnetic state (Table I). For higher cobalt and nickel contents ($x = 0.08$) for the quenched sample with cobalt and slowly cooled sample with nickel, the magnetic transformation was found to be either completely suppressed or shifted to a temperature below 78 K (Figs 1 and 2). Further investigation of these samples and samples with higher cobalt and nickel content at low temperatures ($T < 78\,K$) may help in the explanation of the transformation temperature behaviour.

From the magnetization at 78 and 150 K and the magnetization at 0 K which was determined by extrapolation from the thermomagnetic curves shown in Figs 1 and 2, the magnetic moment, M_T, at 0, 78 and 150 K (M_0, M_{78}, M_{150}) were determined from the relation

$$M_T = A(\sigma_T/N)\mu_B$$

where σ_T is the magnetization at temperature T, N is Avogadros number, μ_B is the Bohr magneton and A is the molecular weight of the sample. In Fig. 3, the cobalt and nickel concentration dependence of the moments M_0, M_{78} and M_{150} is represented. This figure shows that for all samples, the magnetic moment decreased monotonically on increasing the cobalt and nickel concentration from $x = 0.02$ to $x = 0.08$.

According to the ionic arguments, the metal lattice is thought to be populated by Fe^{2+} and Fe^{3+} ions and vacancies □, a random distribution of which leads to a zero magnetization. The reduction of the magnetization arising from the replacement of iron by the transition metal cobalt and nickel was less evident in the slowly cooled samples. The magnetic coupling which occurs during the quenching of the samples on replacing the iron cations by cobalt and nickel leads to a decrease of the magnetic moment of the samples, Fig. 3. This indicates that more or less disordered distributions of Fe^{2+}, Fe^{3+} and vacancies □ among the successive metal layers have been retained by quenching. The effect of thermal history of the sample is more pronounced in the samples which contain nickel, where the slowly cooled samples have nearly twice the values of magnetic moments of the samples obtained by quenching, Fig. 3.

3.2. The paramagnetic region

The relation between the reciprocal susceptibility $1/\chi$ and temperature (T) in the paramagnetic region for

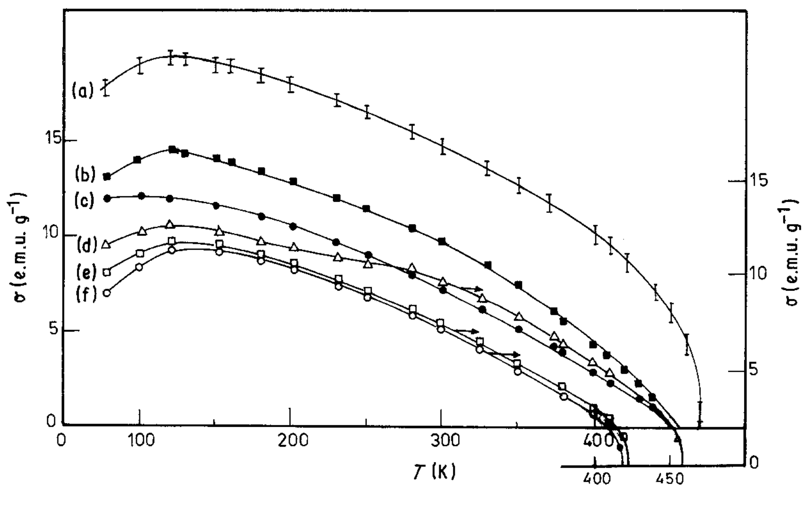

Figure 2 Magnetization–temperature dependence for slowly cooled $(Fe_{1-x}M_x)_7Se_8$ samples. Left-hand axis: (a) M = Ni, $x = 0.02$, (b) M = Ni, $x = 0.05$, (c) M = Ni, $x = 0.08$. Right-hand axis: (d) M = Co, $x = 0.02$, (e) M = Co, $x = 0.05$, (f) M = Co, $x = 0.08$.

TABLE I Values of the transition temperature, T_m, and the Curie temperature, T_c, for the quenched and the slowly cooled samples $(Fe_{1-x}M_x)Se_8$, the molar Curie constant, C_M, and the asymptotic Curie temperature, θ_p

M	x	Quenched samples		Slowly cooled samples		C_M	$K^{-\theta_p}$
		T_m (K)	T_c (K)	T_m (K)	T_c (K)		
Ni	0	130	465	130	465	3.66	1500
	0.02	125	465	130	470	4.18	2631
	0.05	120	430	125	460	2.05	1380
	0.08	108	430	–	455	1.76	1844
Co	0.02	125	465	120	457	3.25	958
	0.05	125	460	120	422	2.66	1876
	0.08	–	440	120	420	4.25	2188

the Fe_7Se_8 is given in Fig. 4. The variation of $1/\chi$ with T consists of a linear portion and a sharp drop at the ferrimagnetic Curie temperature indicating the occurrence of magnetic ordering.

In the magnetic aspect, the behaviour of the alloys with nickel and cobalt is little different from that of the Fe_7Se_8 alloy. No discontinuity was observed in the linear part of $1/\chi - T$ relation, which could be considered an indication of the absence of any structural transition above the ferrimagnetic Curie temperature. The relations of $1/\chi$ against T for all other $(Fe_{1-x})_7Se_8$ samples studied are also shown in Fig. 4. The extrapolation of the linear part of $(1/\chi) - T$ relation to $1/\chi = 0$ gives the asymptotic point, θ_p, for all the samples studied which are given in Table I. The addition of the transition metals cobalt or nickel in small amounts hardly changes the magnetic susceptibility of the host material. Large amounts of cobalt and nickel give rise to a remarkable decrease of the magnetic susceptibility. The low susceptibility values are in good agreement with the observed low susceptibilities of nickel selenides and cobalt alloys [3, 12]. The thermal history of the sample plays no part in the results in the paramagnetic region.

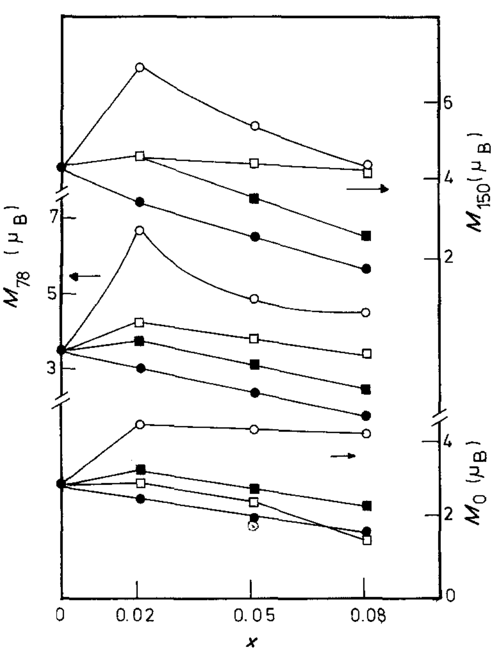

Figure 3 The variation of the magnetic moment in (μ_B) at 0, 78 and 150 K (M_0, M_{78} and M_{150}) with the concentration (x) in the $(Fe_{1-x}M_x)_7Se_8$ samples. (○) S_{Ni}, (□) S_{Co}, (■) q_{Co}, (●) q_{Ni}.

The magnetic susceptibilities are directly related to the magnetic moments. Thus, it is advantageous to focus all attention on the magnetic moment, μ_{eff}, of the samples. The number of the effective Bohr magnetons was calculated from each value of the molar Curie constant, C_M (the Curie constant $C \times$ the molecular weight). Provided that the Lande factor $g = 2$ i.e. the orbital momentum is completely quenched, the effective magnetic moment of the samples decreases with the increasing amount of iron replaced by nickel or cobalt (Fig. 5).

We obtained the spin quantum number, S, by the relation

$$\mu_{eff} = [4S(S+1)]^{1/2} = \left(\frac{3kC}{N}\right)^{1/2}$$

S takes a value near $\frac{5}{2}$ for $x = 0.02$ and near $\frac{3}{2}$ for $x = 0.08$ (Fig. 5).

The two limiting descriptions of transition metal selenides are the ionic concept dealing with the

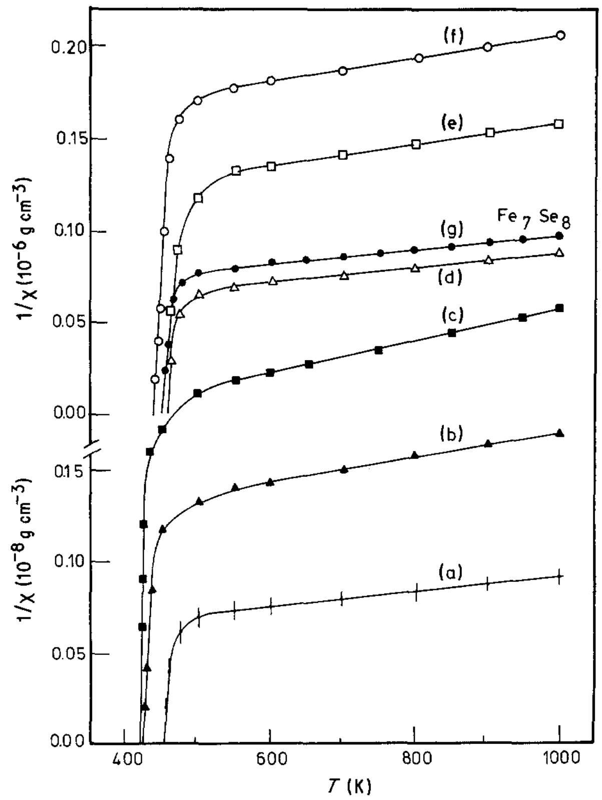

Figure 4 The dependence of the reciprocal susceptibility, $1/\chi$, on temperature for the $(Fe_{1-x}M_x)_7Se_8$ samples. Lower vertical axis: (a) M = Ni, $x = 0.02$, (b) M = Ni, $x = 0.05$, (c) M = Ni, $x = 0.08$. Upper vertical axis: (d) M = Co, $x = 0.02$, (e) M = Co, $x = 0.05$, (f) M = Co, $x = 0.08$, (g) $x = 0$.

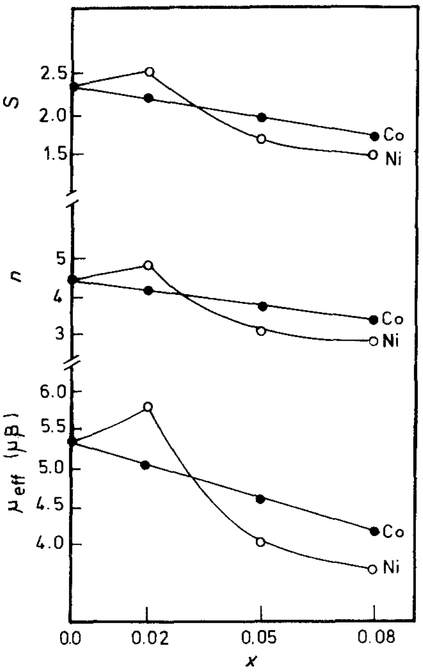

Figure 5 Concentration dependence of the paramagnetic moment, μ_{eff}, the spin quantum number, S, and the number of unpaired electrons, n, in the paramagnetic $(Fe_{1-x}M_x)Se_8$ samples.

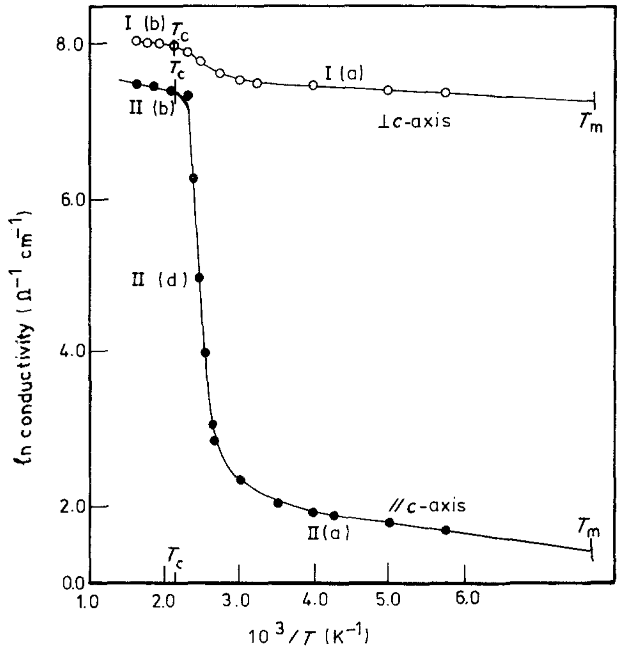

Figure 6 Thermal variation of the electrical conductivity of the sample Fe_7Se_8 with applied electric field. $\perp$ perpendicular to the c-axis, $\parallel$ parallel to the c-axis.

localized moments and the band picture [13]. According to the ionic concept, the Fe_7Se_8 lattice is populated by Fe^{2+} and Se^{2-} ions, and the iron vacancies □ are electrostatically balanced by an appropriate number of Fe^{3+} ions [14]. Provided that Fe^{2+} and Fe^{3+} are substituted by M^{2+} and M^{3+}, we obtained the distribution

$$[Fe^{2+}_{1-x}M^{2+}_{x}]_5\square[Fe^{3+}_{1-x}M^{3+}_{x}]_2[Se^{2-}]_8$$

Accordingly, there are four different contributions with the average Curie constant, $\bar{C}$, given by

$$\bar{C} = \frac{1-x}{7}(5C_{Fe^{2+}} + 2C_{Fe^{3+}}) + \frac{x}{7}(5C_{M^{2+}} + 2C_{M^{3+}})$$

Provided that the metal atoms are in the high spin state as in many transition metal chalcogenides, the calculated values showed poor agreement with the experimental results. We conclude that considering the character of the d-electrons as intermediate between localized and band picture is most likely a suitable description of the present results.

The thermal variations of the electrical conductivity of a single crystal of the host material (Fe_7Se_8), prepared by the method which was explained previously [14], with the applied electric field perpendicular to the c-axis and parallel to the c-axis, are represented in Fig. 6. It may be assumed that the main part of conduction will be caused by the exchange of electrons between Fe^{2+} and Fe^{3+} ions, and the anisotropy and anomaly will be ascribed to the spin correlation of the conduction electrons. According to Kamigdichi *et al.* [15], the direction of antiferromagnetism in Fe_7Se_8 is parallel to the c-axis at temperatures below T_m and is perpendicular to the c-axis at temperatures above T_m and as the temperature rises through the transformation point (T_m) a superexchange interaction between spin pairs decreases. In Fig. 6 in the range of temperature near T_m an easy flow of current takes place along a direction perpendicular to the c-axis (curve Ia) because the spins in this direction are arrayed parallel to each other [15] and a hard flow of current will be expected along the c-axis (curve IIa), because the spins in this direction are arrayed antiparallel to each other [14, 15]. In the temperature range between T_m and T_c the spins are disposed in the c-plane, as mentioned above, and a flow of current along the c-axis increases to the same amount as the flow along a direction perpendicular to the c-axis (region IId). Above T_c the electrons released from antiferromagnetic interaction behave like those in the conduction band and contribute to the metallic conduction (region b, Fig. 6). Similar anomaly in the conductivity behaviour was found in nickel and iron sulphides [6, 16, 17].

Acknowledgement
The author would like to thank Professor V. I. Cherchernikof for his help during the experimental part of this work.

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Received 21 May
and accepted 22 October 1987