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The Magnetic and Thermoelectric Properties of NiAs-type $Fe_{0.89}Se$

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The magnetic structure of NiAs-type $Fe_{1-x}Se$ is made up by two sets of oppositely aligned ferromagnetic layers parallel to the hexagonal (001) plane. The imbalance of the sublattice magnetizations resulting in ferrimagnetism is usually attributed to the ordered arrangement of the metal vacancies. The results of the present paper provide a direct experimental proof of the correlation between the crystallographic order and the magnetic properties. It could not be distinguished whether the observed effects on the magnetization are due to a combined ordering of vacancies and Fe^{3+} ions or to the ordering of the Fe^{3+} ions only. Partial disorder was obtained by quenching samples of $Fe_{0.89}Se$ from temperatures high enough to destroy the ordered arrangement. As inferred from the magnetization data the order parameter varied from 0.83 to 0.47 according to quenching temperatures ranging from 670 K to 1 270 K. In contrast to the magnetization the ferri-antiferromagnetic transformation occurred invariantly at about 170 K irrespective of the different degree of order. The thermoelectric power was positive and increased with decreasing temperature reaching $+49\,\mu VK^{-1}$ at 85 K. The discontinuity observable at about 170 K coincides roughly with the magnetic transformation indicating magnetic contributions to the thermoelectric power.

(Keywords: Ferrimagnetism; Fe-selenides; NiAs*-type phases; Selenides; Thermoelectric power)*

Die magnetischen und thermoelektrischen Eigenschaften von $Fe_{0,89}Se$ *mit* NiAs*-Struktur*

Die magnetische Struktur von $Fe_{0,89}Se$ (NiAs-Typ) besteht aus zwei Sätzen entgegengesetzt gerichteter ferromagnetischer Schichten parallel zur hexagonalen (001)-Ebene. Die Ungleichheit der Magnetisierungen der Untergitter, welche den Ferrimagnetismus verursacht, wird üblicherweise der geordneten Verteilung von Leerstellen zugeschrieben. Die Resultate der vorliegenden Arbeit liefern einen direkten experimentellen Beweis für den Zusammenhang zwischen kristallographischer Ordnung und magnetischen Eigenschaften. Es konnte nicht unterschieden werden, ob die beobachtete Auswirkung auf die Magnetisierung durch die gemeinsame Ordnung der Leerstellen und Fe^{3+}-Ionen

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oder durch die Ordnung der Fe^{3+}-Ionen allein bedingt ist. Durch Abschrecken der Proben von Temperaturen, welche hoch genug waren, um die geordnete Verteilung zu zerstören, wurde eine teilweise Entordnung erhalten. Die Ordnungsparameter, welche aus den Magnetisierungsdaten abgeleitet wurden, variierten von 0,83 bis 0,47, entsprechend den Abschrecktemperaturen von 670 K bis 1270 K. Im Gegensatz zur Magnetisierung vollzog sich die ferri-antiferromagnetische Transformation konstant bei ca. 170 K unabhängig vom unterschiedlichen Ordnungsgrad. Die thermoelektrische Kraft war positiv, nahm mit abnehmender Temperatur zu und erreichte bei 85 K einen Wert von 49 μVK^{-1}. Die Diskontinuität, welche bei 170 K beobachtbar war, fällt mit der magnetischen Transformation zusammen und läßt magnetische Beiträge zur thermoelektrischen Kraft erkennen.

Introduction

The nonstoichiometric NiAs type phase $Fe_{1-x}Se$ is known to be either ferri- or antiferromagnetic[1,2] depending on the iron deficiency x ranging from 0.06 to 0.16 at 823 K (Ref.[3]). Different arrangements of the vacant metal sites give rise to a variety of ordered structures as reported for Fe_7Se_8 (Ref.[4–6]). Because of the layered magnetic structure[7–9] the distribution of the metal vacancies is thought to be of particular importance since it determines the magnetism of $Fe_{1-x}Se$. Two sets of ferromagnetic layers parallel to (001) are oppositely aligned resulting in antiferromagnetism if the vacancies are randomly distributed. In fact, alloys less deficient in iron ($x < 0.10$) are antiferromagnetic, but the magnetic structure has not yet been confirmed. If the vacancies occur in every other metal layer only—this is common to all known superstructures in this system—then the balance of the sublattice magnetizations will be disturbed and ferrimagnetism will appear. This is actually the well established magnetic structure of ferrimagnetic $Fe_{1-x}Se$ ($0.10 \leq x \leq 0.16$) as represented by stoichiometric Fe_7Se_8. $Fe_{0.89}Se$ is of particular interest since at this composition both ferri- and antiferromagnetism are observable. The ferrimagnetic state stable at room temperature transforms into an antiferromagnetic state on cooling below 170 K (Ref.[1]). In this paper additional aspects of the close correlation between the crystallographic and the magnetic structure are elaborated. Especially the influence of thermal treatment on magnetization and the magnetic transformation in $Fe_{0.89}Se$ will be emphasized. Apart from some data on Fe_7Se_8 (Ref.[13]) up to now the variation of the thermoelectric power on passing from the ferri- to the antiferromagnetic state has not been investigated.

Experimental Method

The samples were prepared by alloying appropriate amounts of the pure elements using iron sheet (99.9%, Ferrovac E, Vacuum Metals Corp., Syracuse,

U.S.A.) and selenium shots (99.999% ASARCO, New York, U.S.A.). The mixtures were evacuated at pressures of 0.01 Pa, flushed with Ti-gettered argon, sealed in double quartz capsules and heated at 1270 K for one week. The quenched specimens were ground, sealed under vacuum and homogenized at 870 K for about two weeks. Subsequently different thermal treatments were achieved by annealing the samples once more at different temperatures above 600 K followed by rapid quenching in ice water. The purity was controlled by X-ray analyses in 57.3 mm *Debye-Scherrer* cameras using Co-Kα radiation and Fe-filters. The magnetic measurements were performed on a magnetic balance of the *Faraday* type. The magnetizations refer to a magnetic field of 8030 Oe

Table 1. *Structural and magnetic data of* NiAs-*type* $Fe_{0.89}Se$ *alloys annealed at different temperatures. Last digits uncertain. The order parameters were obtained from Eqs. (11) and (12), respectively*

Annealing temperature T (K)	Lattice constants a (Å)	c (Å)	Magnetization σ (extrap.) (emu/g)	Order parameter $\eta(\square)$, $\eta(3+)$
670	3.632	5.911	7.6	0.83
870	3.632	5.910	7.2	0.78
990	3.634	5.913	6.8	0.74
1120	3.633	5.911	4.7	0.51
1270	3.632	5.910	4.3	0.47

with *Mohr*'s salt used for calibration. The saturation magnetizations were estimated by simple extrapolation towards 0 K; accordingly the last digits are uncertain. The thermoelectric voltage E was measured in helium atmosphere using pure copper as reference material. The temperature difference ΔT between the two sample—copper junctions could be reversed and varied continuously in the range $0 \leq \Delta T \leq 10$ K. The thermoelectric power S (*Seebeck* coefficient) was obtained from the slope of the E vs. ΔT plots evaluated at $\Delta T = 0$ K. Attention was paid to occasional effects arising from the anisotropy by varying the orientation of the sample. A detailed description of the instrumentation is given elsewhere[10].

Results and Discussion

The phase diagram shows $Fe_{0.89}Se$ to be unstable at room temperature[3]; for different thermal treatments the samples were annealed at 670, 870, 990, 1120, and 1270 K, resp. The powder diagrams of the quenched samples were indexed as the hexagonal NiAs-type structure. Since no other phase impurities were indicated, it was concluded that the observed effects are basically those of $Fe_{0.89}Se$. Despite the different thermal treatments the lattice parameters listed in Table 1 were found to be identical within the limits of accuracy. Besides the para-ferrimagnetic transition at 460 K $Fe_{0.89}Se$ undergoes another magnetic

transformation which stabilizes the antiferromagnetic state at the expense of the ferrimagnetic state. Irrespective of the previous thermal treatment this transformation occurs invariantly at 170 K as is evident from Fig. 1. The magnetization on the other hand varies appreciably depending on the thermal treatment. Annealing at higher temperatures tends to decrease the magnetization. A reduced magnetization in turn should be the consequence of a partial vacancy disorder, provided the magnetic structure given in the introduction is basically correct. This implies that the different magnetizations reflect different degrees of order obtained by quenching from the annealing temperature. A quantitative treatment will be attempted by using the ionic concept which has been applied successfully in previous papers[1,2,11]. The basic assumptions are the antiferromagnetic coupling between sublattice A and B and the introduction of formal valencies. In the most general case each sublattice is populated by Fe^{2+} ions, Fe^{3+} ions and vacancies in relative amounts given by $n_A(2+)$, $n_A(3+)$, $n_A(\square)$ and $n_B(2+)$, $n_B(3+)$, $n_B(\square)$. The net magnetic moment per atom μ is determined by the opposite alignment between the moments of the different sublattices:

$$\mu = [n_A(2+) - n_B(2+)]\frac{\mu(2+)}{1-x} + [n_A(3+) - n_B(3+)]\frac{\mu(3+)}{1-x} \tag{1}$$

$\mu(2+)$ and $\mu(3+)$ are the magnetic moments of the Fe^{2+} and Fe^{3+} ions, resp., x refers to the stoichiometry according to the notation $Fe_{1-x}Se$. Introducing the distribution parameters $\eta(2+)$, $\eta(3+)$, $\eta(\square)$

$$\frac{n_A(2+) - n_B(2+)}{n_A(2+) + n_B(2+)} = \eta(2+) \tag{2}$$

$$\frac{n_A(3+) - n_B(3+)}{n_A(3+) + n_B(3+)} = \eta(3+) \tag{3}$$

$$\frac{n_A(\square) - n_B(\square)}{n_A(\square) + n_B(\square)} = \eta(\square) \tag{4}$$

and the total number of Fe^{2+}, Fe^{3+} and vacancies $N(2+)$, $N(3+)$, $N(\square)$, one obtains Equ. (5), which correlates μ with $\eta(2+)$ and $\eta(3+)$:

$$\mu = \frac{N(2+)}{1-x}\mu(2+)\eta(2+) + \frac{N(3+)}{1-x}\mu(3+)\eta(3+) \tag{5}$$

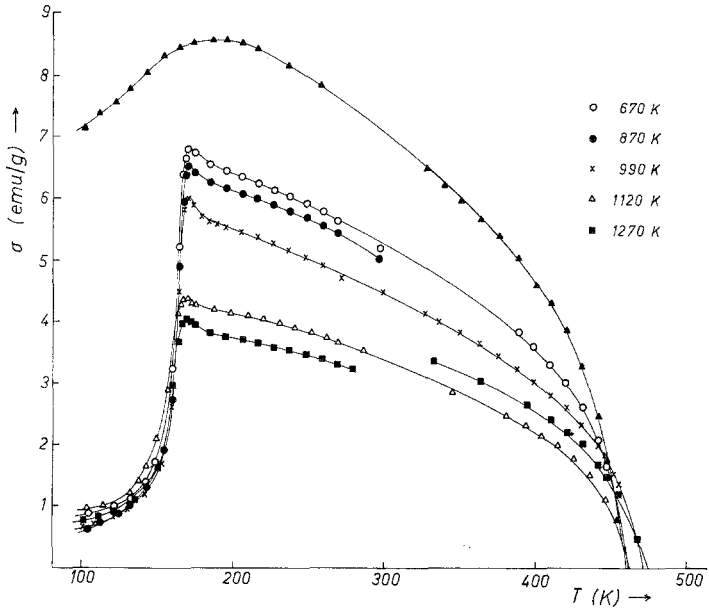

Fig. 1. Magnetization of NiAs-type $Fe_{0.89}Se$ alloys annealed at different temperatures. The discontinuity of the sample quenched from 1270 K (■) is due to the precipitation of tetragonal PbO-type β-FeSe formed by slow cooling. The curve ▲ also refers to a mixture of hexagonal NiAs-type $Fe_{1-x}Se$ and tetragonal PbO type β-FeSe

With

$$n_A(2+) + n_A(3+) + n_A(\square) = 0.5 \tag{6}$$

$$n_B(2+) + n_B(3+) + n_B(\square) = 0.5 \tag{7}$$

we obtain by subtracting Eq. (7) from Eq. (6) and substituting Eqs. (2), (3) and (4) Eq. (8):

$$N(2+)\eta(2+) + N(3+)\eta(3+) + N(\square)\eta(\square) = 0 \tag{8}$$

Assuming that x vacancies are electrostatically balanced by $2x\,Fe^{3+}$ ions and substituting $\eta(2+)$ in Eq. (5) by use of Eq. (8) results in Eq. (9), which gives the correlation between magnetization and crystallographic order.

$$\sigma = \frac{x}{1-x} \left| \mu(2+)\eta(\square) + 2[\mu(3+) - \mu(2+)] \cdot \eta(3+) \right| \cdot Z \tag{9}$$

Based on the assumption that the Fe^{2+} and Fe^{3+} ions carry a magnetic moment of $4\,\mu_B$ and $5\,\mu_B$, Equ. (9) reduces to

$$\sigma = \frac{2x}{1-x} \mid \eta(3+) - 2\eta(\square) \mid Z \cdot \mu_B \tag{10}$$

Z is the number of iron atoms per gram alloy, μ_B is the *Bohr* magneton. In applying Eq. (10) three special cases will be discussed:

a) Sublattice B is fully occupied $[\eta(\square) = 1]$ and the distribution of the Fe^{3+} ions is variable $[-1 \leq \eta(3+) \leq 1]$. Due to the variation of $\eta(3+)$ the magnetization is expected to vary from 9.2 to 27.6 emu/g. This is not compatible with the experiments, since even the highest extrapolated magnetization (7.6 emu/g) is clearly below the predicted minimum value.

b) The vacancies are distributed at random over both sublattices $[\eta(\square) = 0]$ and $\eta(3+)$ is variable within $-1 \leq \eta(3+) \leq 1$. The magnetization is now determined by Eq. (11).

$$\sigma = \frac{2x}{1-x} \mid \eta(3+) \mid Z \cdot \mu_B \tag{11}$$

This implies a maximum magnetization of 9.2 emu/g and a zero magnetization if the Fe^{3+} ions are distributed at random $[\eta(3+) = 0]$. The observed magnetizations are in fact within the predicted range (Tab. 1).

c) The vacancies are electrostatically balanced by an appropriate number of Fe^{3+} ions in the same layer. This implies that $\eta(3+)$ equals $\eta(\square)$, since in this instance $n_A(3+) = 2\,n_A(\square)$ and $n_B(3+) = 2\,n_B(\square)$. Therefore Eq. (10) reduces to

$$\sigma = \frac{2x}{1-x} \mid \eta(\square) \mid Z \cdot \mu_B \tag{12}$$

This case is also in accordance with the experimental results, since Eqs. (11) and (12) are numerically equivalent. Based on the present results it is thus not possible to distinguish between case b and c, which differ in their physical meaning despite the numerical agreement.

In case c the variability of the magnetization is related to the distribution of the vacancies among the alternate layers. The ordering within the single layers has not been taken into account since it does not affect our consideration. The values of η calculated from Eq. (12)

range from 0.47 to 0.83 suggesting that neither extreme $\eta = 1$ nor $\eta = 0$ can be obtained by quenching (Tab. 1). The highest degree of order was achieved by annealing at 670 K, where the major portion of the vacancies (92%) is concentrated in one sublattice. In turn, if case b is the adequate description η refers to the more or less ordered distribution of the Fe^{3+} ions. It is not possible to decide whether the degree of order in the quenched samples refers to the equilibrium distribution at the annealing temperature or not or whether different degrees of order are obtained by cooling through a region where the ordering reaction takes place.

The results explain why in some cases the saturation magnetization of hexagonal $Fe_{1-x}Se$ deviates from the value postulated by the ionic model[1]. Alloys less deficient in iron than Fe_7Se_8 are unstable at room temperature; thus they had to be quenched. The present results show that the observed reduction of the magnetization must be due to a considerable degree of disorder.

The magnetization data taken above room temperature were attained by short heating up to about 500 K and immediate rapid cooling to prevent the decomposition of the samples. Accordingly the onset of ferrimagnetism at about 460 K was not reproducible with sufficient accuracy. On cooling below 550 K single phase $Fe_{0.89}Se$ splits up into a two phase region $Fe_{1-x}Se$ in coexistence with tetragonal PbO-type β-FeSe (Ref.[3]). The effect of the decomposition upon the magnetization was studied by annealing the sample, which had been quenched from 870 K, at about 500 K for one hour. Thermal equilibrium during the magnetic measurements was established by slow cooling. In accordance with the phase diagram the composition of the NiAs-type phase approaches Fe_7Se_8, which basically determines the shape of the magnetization curve since the tetragonal β-phase is weakly paramagnetic[2]. The increase of the magnetization and the slight decrease of the *Curie* temperature result from the change in composition. The gradual decrease of the magnetization on cooling below 200 K indicates a magnetic transformation of the type found in Fe_7Se_8 (Ref.[7–9]).

From electrical resistivity data[12,13] it can be inferred that the transport properties of $Fe_{1-x}Se$ should be classified as metallic, although the simple ionic concept seemed to be a useful formalism to treat the magnetic properties. The diffusion thermopower S of a free electron system is expected to be negative in sign and to vary linearly with the temperature T which is absolutely not the case for $Fe_{0.89}Se$. Similar to Fe_7Se_8 (Ref.[13]) the thermopower is positive in sign throughout the accessible temperature range for both bulk and powdered samples and increases remarkably with decreasing temperature reach-

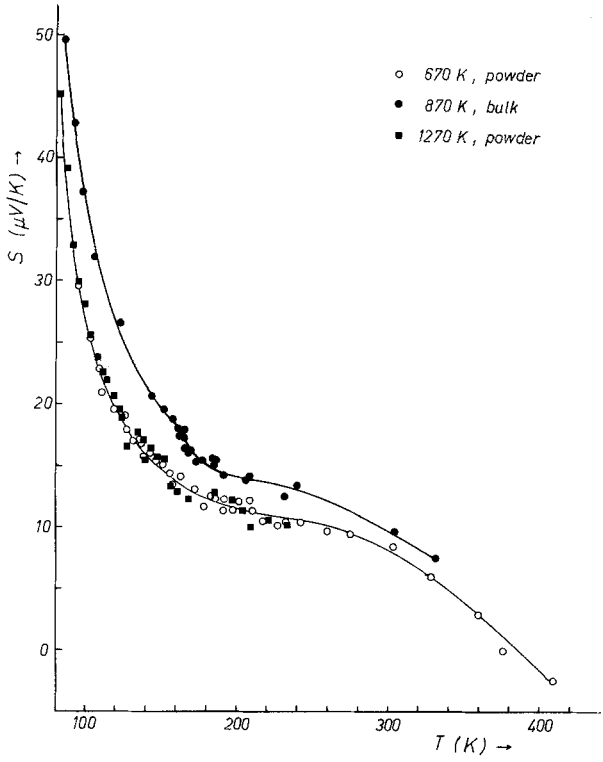

Fig. 2. Thermoelectric power of NiAs-type $Fe_{0.89}Se$ as a function of temperature

ing $+49\,\mu VK^{-1}$ at 85 K (Fig. 2). This is not surprising since many real metals deviate from the free electron behaviour, particularly transition metals and their alloys. Frequently an additional contribution arises from the phonon drag phenomenon which dominates the thermopower at low temperatures. In fact, the actual temperature dependence of the thermoelectric power is indicative of a positive phonon drag contribution which should vary inversely with temperature provided the temperatures are not too low. However, this assumption is not inevitable since the variation of the diffusion part in transition metal alloys is hardly predictable. Despite the variation of the thermal treatment (870 and 1 270 K, resp.) the thermoelectric power was found to be identical within the experimental accuracy. The anomaly of S observed at 170 K in the bulk specimen is less pronounced in the powder sample and has to be assigned to the ferri-antiferromagnetic transition.

It also shows, that besides the unpredictable behaviour of the diffusion thermopower, magnetic effects have to be included in order to account for the thermoelectric properties of magnetic materials.

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