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The Paramagnetic Properties of Iron Selenides With NiAs-Type Structure

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The magnetic properties of the ferrimagnetic iron selenides with NiAs type structure between 51 and 59 at % Se have been investigated using a magnetic balance adapted for measurements up to 800 °C. The magnetic susceptibilities of monoclinic β-$Fe_{1-x}Se$ and hexagonal γ-$Fe_{1-x}Se$ with emphasis on stoichiometric Fe_3Se_4 and Fe_7Se_8 were studied in the paramagnetic region, and from the results phase boundaries and phase transformations derived. The *Curie-Weiss* behaviour of alloys with hexagonal structure permitted the calculation of magnetic moments in the paramagnetic state. The deduced number of unpaired d-electrons n between 50 and 60 at % Se is restricted to the range of $4 < n < 5$ assuming spin-only moments. The magnetic moments and their variation with composition evaluated on the basis of the conventional ionic model were found to be in good agreement with the experimental values.

Paramagnetische Eigenschaften von Eisenseleniden mit NiAs-*Struktur*

Die magnetischen Eigenschaften von ferrimagnetischen Eisenseleniden mit NiAs-Struktur zwischen 51 und 59 At % Se wurden mit einer magnetischen Waage bis 800 °C untersucht. Die magnetischen Suszeptibilitäten von monoklinem β-$Fe_{1-x}Se$ und hexagonalem γ-$Fe_{1-x}Se$ mit besonderer Berücksichtigung von Fe_3Se_4 und Fe_7Se_8 wurden im paramagnetischen Bereich gemessen und von den Resultaten Phasengrenzen und Umwandlungen abgeleitet. Das *Curie-Weiss*-Verhalten der Legierungen mit hexagonaler Struktur erlaubte die Berechnung magnetischer Momente im paramagnetischen Zustand. Die daraus abgeleitete Zahl ungepaarter d-Elektronen zwischen 50 und 60 At % Se unter der Annahme von reinen Spinmomenten beschränkt sich auf $4 < n < 5$. Mit Hilfe des konventionellen ionischen Modells berechnete magnetische Momente und ihre Konzentrationsabhängigkeit stimmen gut mit den experimentellen Werten überein.

Introduction

Although the Fe-Se phase diagram has been studied repeatedly, the phase boundaries are still not well established. In the course of a combined thermoanalytical and thermodynamic investigation it was

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therefore decided to make some additional magnetic measurements, especially in the region of the NiAs-type nonstoichiometric phases, to gain information on the phase boundaries. While the results of the thermoanalytical and thermodynamic investigations will be reported elsewhere, a short account of the magnetic measurements will be given in the present paper.

The two NiAs-type phases, hexagonal Fe_7Se_8 (γ-$Fe_{1-x}Se$) and monoclinic Fe_3Se_4 (β-$Fe_{1-x}Se$), have been studied by numerous investigators, and their ferrimagnetism in connection with the ordered arrangement of vacancies is well etablished[1–16]. Both susceptibility measurements on powders[1–5] in the para- and ferrimagnetic regions and magnetic torque measurements on single crystals[6–8] were carried out. In two other publications[9,10] a theoretical treatment of the magnetic anisotropy of Fe_7Se_8 was given. The magnetic structures of the stoichiometric compositions Fe_7Se_8 and Fe_3Se_4 were studied repeatedly by neutron diffraction[11–16]. The crystal structures of the stoichiometric iron selenides, especially the superstructures of Fe_7Se_8, were extensively analyzed by X-ray diffraction[17–19]. Measurements of electrical conductivity[3,20,21] were mainly carried out in the ferrimagnetic region.

Most of the investigations mentioned above were restricted to the stoichiometric compositions Fe_7Se_8 and Fe_3Se_4, and the influence of the variation of the Se-content was largely neglected. In the present study the effect of composition and temperature on the magnetic properties of the NiAs-type phase was investigated and the phase boundaries of β-$Fe_{1-x}Se$ and γ-$Fe_{1-x}Se$ determined.

Experimental Method

The specimens were prepared by direct synthesis starting with pure 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 components (total amount ~ 2 g) were weighed to within ± 0.1 mg and placed into a quartz capsule which was repeatedly evacuated and flushed with gettered Ar and finally sealed under vacuum (~ 10^{-5} torr). The samples had to be sealed doubly since the quartz capsules cracked on cooling or quenching. The ampoules were heated in vertical resistance-heated and temperature-controlled furnaces up to 1,000 °C, kept about 8 days at temperature, and then quenched in ice water. The specimens were comminuted, sealed once more under vacuum, and homogenized at 600 °C for about two weeks. After quenching the phase composition of the alloys was checked by X-ray analysis. The patterns were obtained with a 57.29 mm *Debye-Scherrer* camera using CoK_α radiation and an Fe-filter.

For the susceptibility measurements the specimens were placed in quartz capsules which were then evacuated and sealed. The magnetic measurements were performed with a *Faraday*-type magnetic balance at magnetic field strengths of 3,880, 6,090, and 8,030 Oe. The samples could be electrically heated up to 800 °C. The temperature was measured by a *Pallaplat*-thermocouple

(RtRh+AuPdPt) which was calibrated at the melting points of high purity Cd, Zn, and Sb. In addition the thermocouple was controlled before and after each measurement by determining the *Curie*-point of Fe and Ni. After thermal equilibrium was established the samples were slowly cooled and for each measurement the temperature was kept constant for about 15 to 30 minutes until the readings remained constant.

As a reference substance *Mohr*'s salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$) with a susceptibility of $32.31 \cdot 10^{-6}$ emu g^{-1} at 20 °C was used. Nearly all monoclinic β-$Fe_{1-x}Se$ alloys contained traces of Fe_3O_4 ($< 0.1\,\%$) which affected the results below the *Curie*-temperature of Fe_3O_4 (585 °C). In the hexagonal region only the Fe-rich alloys with 51.0 and 51.5 at % Se showed small amounts of Fe_3O_4; for all other compositions the susceptibility was independent of the magnetic field strength in the entire range of temperature. The ferrimagnetic contribution of Fe_3O_4 was corrected for by extrapolation for $H \to \infty$.

The experimental susceptibility data were not corrected for the diamagnetic contribution since it is compensated to an unknown extent by a paramagnetic contribution of the conduction electrons[22]. The magnetic moments were calculated from the *Curie*-constants taken from a graphical presentation of $1/\chi = (T - \Delta)/C$. The number of unpaired electrons was obtained from the equation

$$\mu = \sqrt{n\,(n+2)}\;\mu_B.$$

Experimental Results and Discussion

The reciprocal susceptibility values are plotted as a function of temperature in Fig. 1. The different magnetic behaviour of the various phases allowed to determine transformation temperatures and phase boundaries (listed in Fig. 2 and Table 1). The relationships between the phases α, γ, β, and ε between 48 and 62 at % Se and between 200 and 800 °C are shown in the partial phase diagram (Fig. 2)*. At 600 °C the hexagonal γ-phase has a range of homogeneity from 50 to about 55.5 at % Se followed by the monoclinic β-phase with the Se-rich boundary at about 61 at % Se. At the present the question whether γ and β are separated by a two-phase field γ + β or whether γ transforms directly into β cannot be resolved. This problem shall be treated later after completion of the thermoanalytical and thermodynamic investigations. The magnetic studies seem to point towards the existence of a two-phase field between γ and β. At lower temperatures Fe-rich γ is coexisting with the α-phase with PbO-structure and an almost stoichiometric composition of about 49.0 at % Se. With decreasing temperature the range of homogeneity of the γ-phase decreases to the stoichiometric composition Fe_7Se_8 (53.33 at % Se). The Se-rich β-phase is at lower temperature in equilibrium with ε ($FeSe_2$) with marcasite structure.

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* The somewhat irregular sequence of symbols for the various phases most commonly employed in literature has been retained to avoid confusion.

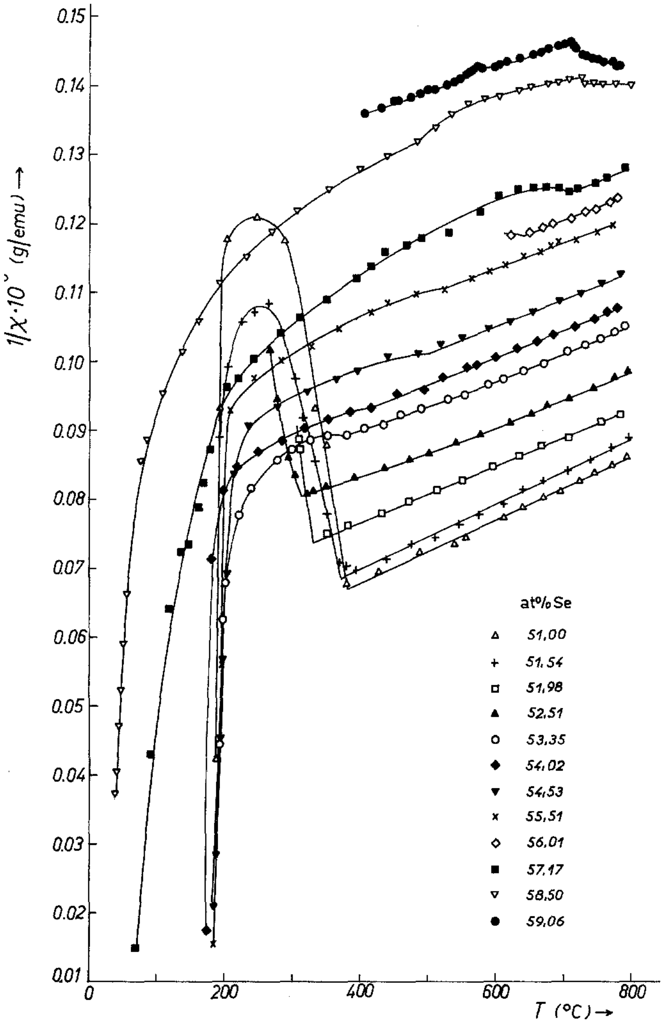

Fig. 1. Reciprocal magnetic susceptibility of NiAs-type iron selenides as a function of temperature

The paramagnetic susceptibilities of β and γ (Fig. 1) are rather similar but a linear relationship between $1/\chi$ and T could only be found for the alloys of hexagonal γ. The α-phase is described as weakly paramagnetic[2] and ε ($FeSe_2$) as diamagnetic[23]. The $\gamma/(\gamma + \alpha)$ phase boundary is clearly indicated by the temperature dependence of the specimens with 51.00, 51.54, 51.98, and 52.51 at% Se because of the low

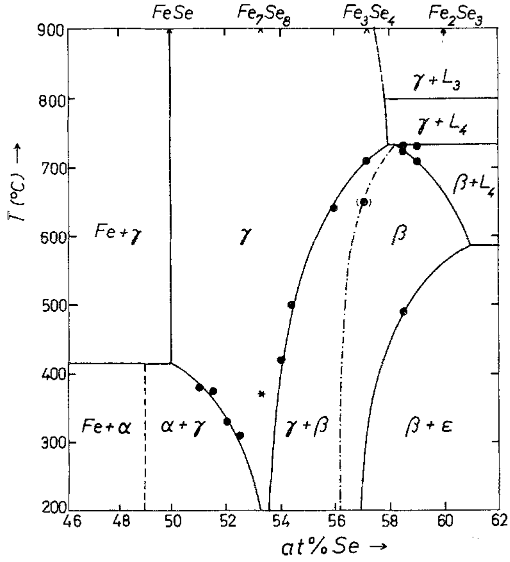

Fig. 2. Partial Fe-Se phase diagram (● phase boundaries and *λ-transformation determined by magnetic susceptibility measurements)

Table 1. *Phase boundaries and Curie-temperatures of* NiAs-*type iron selenides*

Composition (at % Se)		Phase boundaries (°C)	(phases)	*Curie*-temperature (°C)
51.00	$Fe_{0.96}Se$	380	$\gamma/(\alpha+\gamma)$	184
51.54	$Fe_{0.94}Se$	375	$\gamma/(\alpha+\gamma)$	175
51.98	$Fe_{0.92}Se$	330	$\gamma/(\alpha+\gamma)$	—
52.51	$Fe_{0.90}Se$	310	$\gamma/(\alpha+\gamma)$	—
53.35	$Fe_{0.87}Se$	370	$1c \rightleftharpoons 3c$	180
54.02	$Fe_{0.85}Se$	420	$\gamma/(\gamma+\beta)$	172
54.53	$Fe_{0.83}Se$	500	$\gamma/(\gamma+\beta)$	180
55.51	$Fe_{0.80}Se$	—	—	182
56.01	$Fe_{0.79}Se$	640	$\gamma/(\gamma+\beta)$	—
57.17	$Fe_{0.75}Se$	710	$\gamma/(\gamma+\beta)$	65
58.53	$Fe_{0.71}Se$	730	$\gamma+L_4 \rightleftharpoons \beta$	30
		725	$(\beta+L_4)/\beta$	
		490	$\beta/(\beta+\varepsilon)$	
59.06	$Fe_{0.69}Se$	730	$\gamma+L_4 \rightleftharpoons \beta$	
		710	$(\beta+L_4)/\beta$	—

paramagnetic susceptibility of the α-phase. The magnitude of the reduction of χ depends on the mass ratio of α to β and is most pronounced at 51.00 at % Se. At lower temperatures the specimens show a rapid increase in χ which is due to the paramagnetic—ferrimagnetic transition at ~ 179 °C. The phase boundary between the γ- and (γ + β)-phase fields at 710 °C is distinctly recognizable only for the specimen with 57.17 at% Se (Fe_3Se_4). In the case of a direct $\gamma \rightarrow \beta$ transformation it would be very difficult to explain that χ for this alloy remains nearly constant between 710 and 650 °C and increases below 650 °C with decreasing temperature. In the χ-T curves of the alloys with 54.02, 54.53, 55.51, and 56.01 at% Se the $\gamma/(\gamma + \beta)$ phase boundary is hardly visible since even pure hexagonal

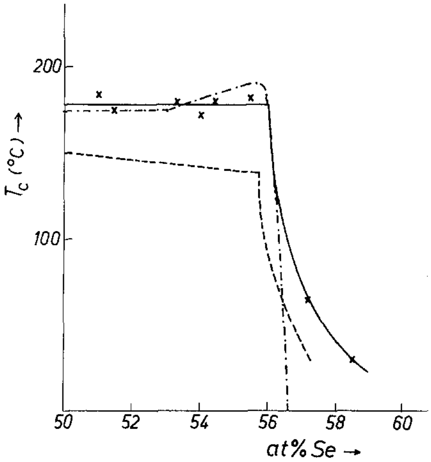

Fig. 3. *Curie*-temperatures of NiAs-type iron selenides (× ——— this investigation, - - - *Hirone et al.*[1], -·-·- *Hirone* and *Chiba*[2])

specimens (53.35 and 52.51 at%Se) show slight deviations from the linear relationship between $1/\chi$ and T. In the alloy with 53.35 at%Se (Fe_7Se_8) a magnetic effect was observed at 370 °C which is most probably connected with the ordering of vacancies. According to *Okazaki*[19] Fe_7Se_8 shows a transition from the 1c—to the 3c—structure between 360 and 375 °C. *Grønvold*[24] found a λ-transition in Fe_7Se_8 at 365 °C which he also interpreted as being due to a structural transition. The two alloys richest in Se (58.50 and 59.06 at%Se) show breaks in the χ-T curve at 730 °C (peritectic reaction $\gamma + L_4 \rightleftharpoons \beta$), at 725 and 710 °C, resp. ($\beta/(\beta + L_4)$ phase boundary), and at 490 °C ($\beta/(\beta + \varepsilon)$ phase boundary at 58.50 at% Se). The effect at 570 °C in the specimen with 59.06 at% Se is probably due to non-equilibrium conditions (peritectic reaction $\beta + L_4 \rightleftharpoons \varepsilon$).

In the paramagnetic range of the γ-phase the susceptibility decreases smoothly with increasing Se-content (at 750 °C from $12.0 \cdot 10^{-6}$ emu g^{-1} at 51 at%Se to $7.5 \cdot 10^{-6}$ emu g^{-1} at 58 at%Se). The concentration dependence of the *Curie*-temperature is shown in Fig. 3 and compared with the results of *Hirone et al.*[1] and *Hirone* and *Chiba*[2]. Between 51 and 56 at % Se the temperature of the paramagnetic-ferrimagnetic transition is constant (~ 179 °C) and then drops sharply with increasing Se-content. One can therefore assume that below 200 °C all specimens between 50 and 56 at % Se contain γ of practically invariable composition, i.e. that at this temperature the ($\alpha + \gamma$)- and ($\gamma + \beta$)-two-phase regions are separated by a very narrow range of homogeneity (~ 0.2at %) centering around Fe_7Se_8 (53.3 at % Se). The *Curie*-temperature between 50 and 56 at % Se is in good agreement with the values for stoichiometric Fe_7Se_8 reported in literature[1–3, 6, 8, 19]: From susceptibility measurements *Hirone et al.*[1] and *Serre et al.*[3] obtained 150 and 182 °C, resp.; from specific heat curves *Hirone* and *Chiba*[2] deduced 174 °C; dilatometric measurements by *Hirakawa*[6] resulted in an anomaly at 170 °C; and *Kamimura et al.*[8] and *Okazaki*[19] reported 176 and 187 °C, resp. Alloys between 56 and 57 at % Se are one-phase (monoclinic β) and also ferrimagnetic but with a lower *Curie*-temperature. *Hirone et al.*[1] found the magnetic transformation of Fe_3Se_4 (57.17 at %Se) at 30 °C, *Serre et al.*[3] at 50 °C. We obtained a *Curie*-temperature of 65 °C at 57.17 at %Se. Again, the concentration dependence of the *Curie*-temperature in Fig. 3 would be very difficult to explain by a direct $\gamma \rightarrow \beta$ transformation.

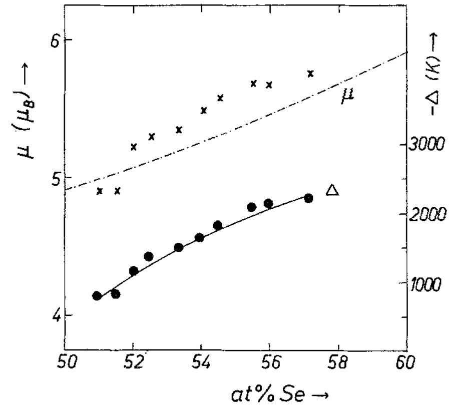

Fig. 4. Magnetic moments (×) and *Weiss* constants (●) of hexagonal γ-$Fe_{1-x}Se$ as a function of composition (--- magnetic moments calculated using the ionic model)

The concentration dependence of the magnetic moment and of the *Weiss* constant is shown in Fig. 4 and Table 2. Both quantities increase with increasing Se content. *Maxim*[5] reported for an alloy with 51 at % Se a *Weiss* constant $\Delta = -1{,}245\,\mathrm{K}$ and $\mu = 5.57\,\mu_B$, and for an alloy with 53.7 at% Se $\Delta = -1{,}810\,\mathrm{K}$ and $\mu = 5.87\,\mu_B$.

The ferrimagnetism of stoichiometric Fe_7Se_8 and Fe_3Se_4 is usually interpreted by an ionic model although both phases exhibit a more metallic behaviour[3, 20, 21]. The results of various magnetic investigations have indeed put the applicability of this model in question. Neither the magnetic moment in the ferrimagnetic state[13, 14, 16], nor the saturation magnetization of Fe_3Se_4 could be explained. The present study offers for the first time the opportunity to test the ionic model in the paramagnetic range by comparing the experimental magnetic moments with the moments derived from the model. The basic assumption of the ionic model is that by subtraction of Fe^{2+} ions from every second metal atom layer normal to the c-axis metal vacancies and Fe^{3+} ions are formed in the metal sublattice. For the calculation of the magnetic moments it is advantageous to replace the formula $Fe_{1-x}Se$ by $Fe^{3+}_{2x}\,Fe^{2+}_{1-3x}\square_x\,Se^{2-}$ with the distribution of Fe^{2+}, Fe^{3+}, and vacancies over the metal sublattice the paramagnetic range being of no particular significance.

Table 2. *Paramagnetic properties of hexagonal* NiAs-*type iron selenides*

Composition at % Se		Magnetic moment theoret. μ (μ_B)	exp.	Unpaired electrons n	*Weiss*-constants Δ (K)
51.00	$Fe_{0.96}Se$	4.89	4.98	3.99	—792
51.54	$Fe_{0.94}Se$	4.90	5.03	4.00	—824
51.98	$Fe_{0.92}Se$	5.23	5.07	4.33	—1177
52.51	$Fe_{0.90}Se$	5.29	5.12	4.39	—1336
53.35	$Fe_{0.87}Se$	5.35	5.19	4.44	—1490
54.02	$Fe_{0.85}Se$	5.48	5.25	4.57	—1663
54.53	$Fe_{0.83}Se$	5.57	5.30	4.66	—1830
55.51	$Fe_{0.80}Se$	5.69	5.40	4.77	—2092
56.01	$Fe_{0.79}Se$	5.66	5.46	4.75	—2167
57.17	$Fe_{0.75}Se$	5.76	5.58	4.85	—2223

For $x = 0$ (FeSe) and $x = {}^1/_3$ (Fe_2Se_3) the theoretical spin moments of Fe^{2+} (d^6) and Fe^{2+} (d^5), resp., are to be expected. For all other compositions between $0 < x < {}^1/_3$ the magnetic moments can be obtained by the following equation:

$$\mu = \frac{2x\cdot\sqrt{35} + (1-3x)\cdot\sqrt{24}}{(1-x)}$$

Thus calculated magnetic moments are also listed in Table 2 and plotted in Fig. 4. The calculated moments agree with the experimental results within a few percent and both sets of data show an increase with increasing Se-content. This agreement is surprising since as mentioned above similar calculations in the ferrimagnetic region have led to considerable difficulties.

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