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The Antiferromagnetic and Ferrimagnetic Properties of Iron Selenides With NiAs-Type Structure

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The magnetic properties of the NiAs-type iron selenides have been investigated by susceptibility measurements between 100 and 450 K. Hexagonal γ-$Fe_{1-x}Se$ exhibits both antiferromagnetism and ferrimagnetism depending on composition. For antiferromagnetic alloys with $0.02 \leqslant x \leqslant 0.10$ (50.5 to 52.5 at % Se) the transition to the paramagnetic state is assumed to occur in the unstable range between room temperatur and about 573 K. Ferrimagnetism is observed at compositions near Fe_7Se_8 ($0.10 \leqslant x \leqslant 0.16$; 52.5 to 54.3 at % Se) with *Curie* temperatures varying only slightly with composition. In Fe_7Se_8 the ferri-paramagnetic transition is observable at 453 K. The characteristic discontinuities in the magnetization curves of Fe_7Se_8 in both superstructures (3*c*, 4*c*) are related to the rotation of the magnetic moments from a direction close to [001] into (001).

The antiferromagnetism of $Fe_{0.89}Se$ (52.8 at % Se) changes abruptly into ferrimagnetism when the temperature is raised above 160 K. The similar abrupt changes of the magnetic susceptibilities in the antiferromagnetic region are possibly associated with a crystallographic transformation. In the range of monoclinic β-$Fe_{1-x}Se$ with $0.24 < x < 0.36$ (56.8 to 61.0 at % Se) only Fe_3Se_4 is ferrimagnetic above room temperature; alloys containing more selenium are ferrimagnetic far below room temperature. In $Fe_{0.69}Se$ (59.1 at % Se) the transition from ferrimagnetism to paramagnetism was observed at 145 K. The saturation magnetization and the magnetic moments obtained from neutron diffraction are compared with values calculated from a simple ionic model.

Die antiferromagnetischen und ferrimagnetischen Eigenschaften von Eisenseleniden mit NiAs-*Struktur*

Die magnetischen Eigenschaften von Eisenseleniden mit NiAs-Struktur wurden mittels Suszeptibilitätsmessungen zwischen 100 und 450 K untersucht. Hexagonales γ-$Fe_{1-x}Se$ zeigt abhängig von der Konzentration sowohl Antiferromagnetismus als auch Ferrimagnetismus. In antiferromagnetischen Legierungen mit $0,02 \leqslant x \leqslant 0,10$ (50,5 bis 52,5 At % Se) verläuft die Umwandlung in den paramagnetischen Zustand im nichtstabilen Bereich zwischen Raumtemperatur und ≈ 573 K. Ferrimagnetismus wurde in der Nähe von Fe_7Se_8 ($0,10 \leqslant x \leqslant 0,16$; 52,5 bis 54,3 At % Se) beobachtet mit *Curie*temperatu-

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ren, die sich nur wenig mit der Konzentration ändern. Fe_7Se_8 zeigt die ferri-paramagnetische Umwandlung bei 453 K. Die charakteristischen Diskontinuitäten der Magnetisierungskurven von Fe_7Se_8 in beiden Überstrukturen (3fache und 4fache c-Achse) hängen mit der Drehung der magnetischen Momente aus einer [001]-nahen Richtung in die (001)-Ebene zusammen. Der Antiferromagnetismus von $Fe_{0,89}Se$ (52,8 At% Se) geht bei 160 K sprunghaft in Ferrimagnetismus über. Ähnliche sprunghafte Änderungen der magnetischen Suszeptibilitäten im antiferromagnetischen Bereich sind möglicherweise mit einer kristallographischen Umwandlung verbunden. Im Phasenbereich von monoklinem β-$Fe_{1-x}Se$ mit $0,24 \leqslant x \leqslant 0,36$ (56,8 bis 61,0 At% Se) ist einzig Fe_3Se_4 oberhalb Raumtemperatur ferrimagnetisch; Legierungen mit mehr Selen sind weit unterhalb Raumtemperatur ferrimagnetisch. In $Fe_{0,69}Se$ (59,1 At% Se) wurde der Übergang von Ferri- zu Paramagnetismus bei 145 K beobachtet. Die Sättigungsmagnetisierung und die magnetischen Momente aus Neutronenbeugungsexperimenten wurden mit Werten verglichen, die mit einem einfachen ionischen Modell berechnet wurden.

Introduction

The magnetic[1–17], electrical[4, 18, 19], and crystallographic[20–22] properties of the NiAs-type iron selenides γ-$Fe_{1-x}Se$ ($\approx Fe_7Se_8$) and β-$Fe_{1-x}Se$ ($\approx Fe_3Se_4$) have been already investigated by a great number of authors. In a previous publication[1] the magnetic behavior of the hexagonal γ-phase and the monoclinic β-phase was studied in the paramagnetic range. By varying the composition and temperature several phase boundaries were determined in the Fe—Se system. Theoretical magnetic moments based on an ionic model which was sometimes used for Fe_7Se_8 and Fe_3Se_4 agreed within a few percent with the experimental values. Magnetic moments of Fe_3Se_4 for the ferrimagnetic range, obtained from neutron diffraction[14, 15, 17] and saturation magnetization[2, 5, 7, 10], however, did not agree with the model calculations. Ferrimagnetic *Curie* temperatures of Fe_7Se_8 and Fe_3Se_4 determined by different methods are in agreement and are reported to be ~ 450 K and 320 K, resp.[2–4, 7, 9, 22]. *Curie* temperatures at other compositions are put in doubt by the phase diagram[23] since many alloys between 50 and 61 at% Se are stable only in the paramagnetic range far above the *Curie* temperature. Neutron diffraction studies of Fe_7Se_8 revealed an additional magnetic transformation which occurs discontinuously or continuously depending on the type of superstructure. So far no effect of this transformation on the magnetization of Fe_7Se_8 has been observed.

Experimental Method

Specimens were prepared by alloying pure iron sheet (99.9%, Ferrovac E, Vacuum Metals Corp., Syracuse, USA) and selenium shots (99.999%, ASARCO, New York, USA). Details of the specimen preparation and of the magnetic measurements can be found in a previous publication[1]. After quenching the samples from 600 °C they were comminuted, and diluted with quartz powder for measurements in the ferrimagnetic range. Alloys with the composition Fe_7Se_8 were heat treated at 320 °C to form the 3c—superstructure, and at 230 °C to obtain the 4c—superstructure. Measurements above room temperature were carried out very quickly with cooling rates from 10 to 15 °C/min to avoid phase transformations in metastable samples. Magnetizations are generally referred to a magnetic field strength of 8030 Oe; in the antiferromagnetic region additional measurements were carried out at 6090 and 3880 Oe. Saturation magnetization was obtained graphically by extrapolation of the temperature towards 0 K.

Results and Discussion

The magnetic properties of the NiAs-type iron selenides were found to be strongly composition dependent. In addition to already known ferrimagnetic alloys antiferromagnetic behavior was observed for the first time. A similar change in magnetic order caused by a change in composition was found in the Fe—S system by *Haraldsen*[24] in the range FeS—Fe_7S_8 and later confirmed by *Lotgering*[25]. In view of the varied magnetic behavior it seems reasonable to divide the entire region of NiAs-type iron selenides in four parts. This partial magnetic phase diagram based on samples quenched from 600 °C is shown in Fig. 1. Hexagonal γ-$Fe_{1-x}Se$ in the Fe-rich range $0.02 \leqslant x \leqslant 0.10$ (50.5 to 52.5 at % Se) exhibits a magnetic behavior characteristic of antiferromagnetic substances below the *Néel* temperature (Fig. 2). The magnetic susceptibilities of the alloys $Fe_{0.92}Se$ (52.0 at % Se) and $Fe_{0.91}Se$ (52.3 at % Se) were nearly independent on the magnetic field strength and increased with increasing temperature. The *Néel* points, situated above room temperature in the metastable part of the phase, could not be observed. All antiferromagnetic samples showed a discontinuous change of the susceptibility at the temperature T_0 (Fig. 2, Table 1) which was especially pronounced at 52.5 at % Se ($Fe_{0.90}Se$). The susceptibility of this alloy which lies at the border to the ferrimagnetic range was already noticeably dependent on the magnetic field strength above T_0 (186 K). Similar discontinuities have been observed previously in iron sulfides at various compositions[24, 26–28] and have been associated with the simultaneous formation of a superstructure with ordered vacancies. Presumably the anomalies in antiferromagnetic iron selenides are caused by a similar crystallographic transformation whereby the antiferromagnetic character is preserved (the possibility of explaining these anomalies by the presence of oxide impurities has been ruled out). In case of an ordered structure the vacancies have to be distributed in equal parts between the magnetic sublattices; for a completely disordered distribution of vacancies this condition is *eo ipso* fulfilled.

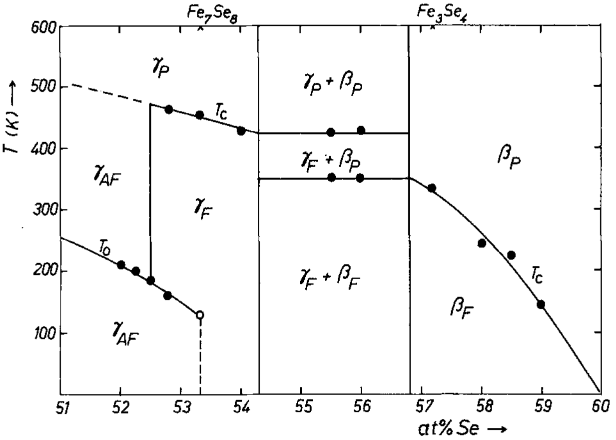

Fig. 1. Magnetic phase diagram in the region of NiAs-type iron selenides based on samples quenched from 873 K (P: paramagnetic, AF: antiferromagnetic, F: ferrimagnetic)

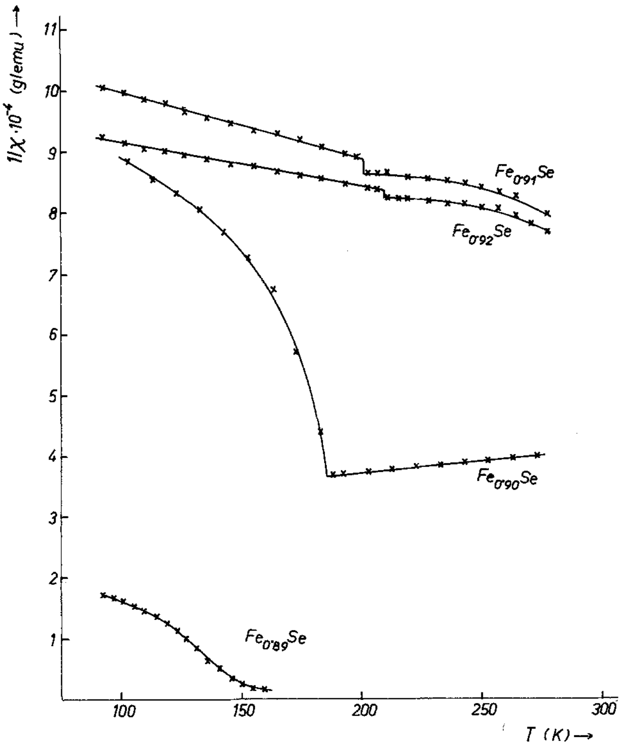

Fig. 2. Reciprocal magnetic susceptibilities of antiferromagnetic iron selenides with NiAs-structure as function of temperature

In the ferrimagnetic range of hexagonal γ-$Fe_{1-x}Se$ ($0.10 \leqslant x \leqslant 0.16$, i.e. 52.5 to 54.3 at % Se) the same transformation causes an abrupt increase of magnetization which ends at T_0 (Fig. 3). $Fe_{0.89}Se$ (52.8 at % Se) is ferrimagnetic above 160 K, at lower temperatures, however, antiferromagnetic. Magnetic transformations of this type which are known for quite some time in the case of iron sulfides in the range $0.07 < x < 0.10$ (51.8 to 52.6 at % S)[24, 25, 29, 30] are classified according to *Haraldsen*[24] as anti-*Curie* transformations. *Lotgering*[25] explained the change from antiferromagnetism to ferrimagnetism by the ordering of vacancies, the antiferromagnetic state stable at lower temperatures being characterized by a statistical distribution. *Hirone et al.*[29] on the other hand assumed another superstructure below the anti-*Curie* temperature in which the vacancies are distributed in equal parts in an ordered manner between the magnetic sublattices. This means for the hexagonal iron selenide that an ordered antiferromagnetic structure is stable below the transformation temperature T_0. The discontinuities in the range $0.02 \leqslant x \leqslant 0.10$ (50.5 to 52.5 at % Se) are caused by randomization of vacancies. Ferrimagnetic iron selenides like $Fe_{0.89}Se$ (52.8 at % Se) remain ordered also above T_0 but in a different form. In case of crystallographic disorder below T_0 as assumed by *Lotgering*[25] for iron sulfides the crystallographic transformation in the range $0.02 < x \leqslant 0.10$ (50.5 to 52.5 at % Se) would be of the order-disorder type with the ordered structure stable above T_0. However, there are no

Table 1. *Magnetic transformations of antiferromagnetic and ferrimagnetic iron selenides with* NiAs *structure*

Composition (at % Se)		Phase	Transformation temperature T_c (K)	T_0 (K)
51.98	$Fe_{0.92}Se$	γ	—	209
52.27	$Fe_{0.91}Se$	γ	—	201
52.51	$Fe_{0.90}Se$	γ	—	186
52.80	$Fe_{0.89}Se$	γ	462	160
53.35	$Fe_{0.87}Se$	γ (Fe_7Se_8)	453	130
54.02	$Fe_{0.85}Se$	γ	430	—
55.51	$Fe_{0.80}Se$	$\gamma + \beta$	426, 350	—
56.01	$Fe_{0.79}Se$	$\gamma + \beta$	429, 350	—
57.17	$Fe_{0.75}Se$	β (Fe_3Se_4)	335	—
57.97	$Fe_{0.73}Se$	β	246	—
58.53	$Fe_{0.71}Se$	β	225	—
59.06	$Fe_{0.69}Se$	β	145	—

indications for an ordered structure in the range $0.02 \leqslant x \leqslant 0.10$ at room temperature.

In Fe_7Se_8 (53.35 at % Se) of the 3c-type a strong increase in magnetization was observed between 100 and 130 K but it could not be ascertained whether the magnetization below 100 K disappears completely or is partially retained. This magnetic transformation has already been found by neutron diffraction[12, 13, 16], electrical conductivity measurements[4, 19], and torsion studies on single crystals[7, 9].

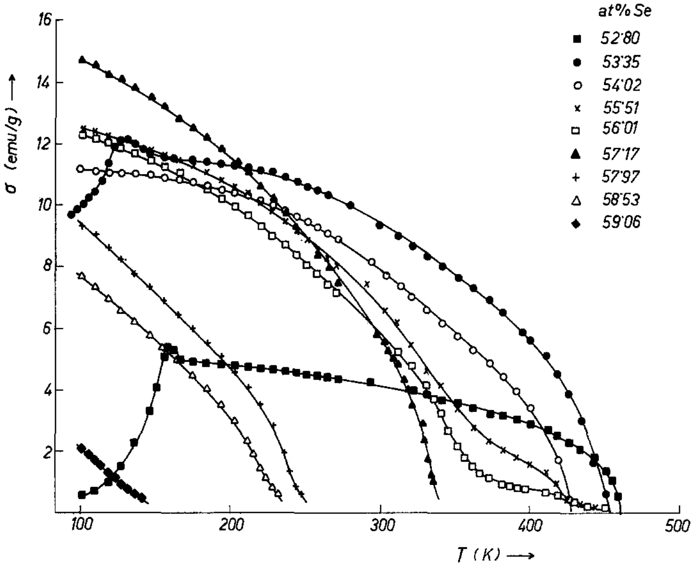

Fig. 3. Magnetization of ferrimagnetic iron selenides with NiAs-structure as function of temperature

In contrast to all other alloys between FeSe and Fe_7Se_8 the magnetic anomaly of Fe_7Se_8 seems not to be caused by a crystallographic transformation according to literature[7, 12, 13, 16] since nowhere a simultaneous change of crystallographic order of Fe_7Se_8 is mentioned. According to neutron diffraction studies[12, 13, 16] the magnetic transformation in Fe_7Se_8 is due to a rotation of the magnetic moments from an original direction close to [001] into the (001) plane. This directional change occurs in the hexagonal 3c-structure abruptly between 120 and 130 K but starts in the triclinic 4c-structure way below 100 K and is complete only at 220 K. Accordingly the magnetization of both the 3c- and 4c-structure is expressed by a pronounced maximum at 130 K and a flat maximum at 220 K, resp. (Fig. 4). $Fe_{0.85}Se$ (54.0 at % Se) was the only hexagonal alloy which at least above 100 K did not exhibit any discontinuities. The *Curie* temperatures in the hexagonal NiAs-type range of homogeneity shown in table as T_c decrease with increasing Se content. The ferri—to paramagnetic transformation of Fe_7Se_8 takes place at 453 K independent on the type of superstructure and in agreement with the data reported for the paramagnetic range[1]. Magnetic measurements of *Hirone et al.*[2] and *Serre et al.*[4] on powders,

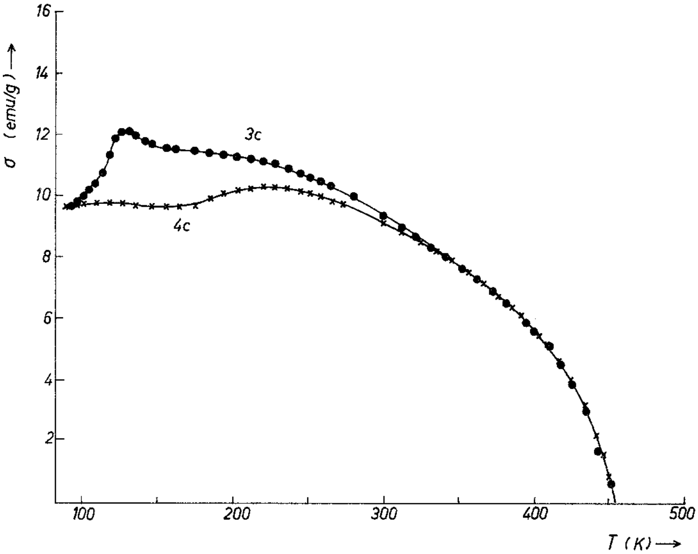

Fig. 4. Magnetization of Fe_7Se_8 with 3 *c*—and 4 *c*—superstructure as function of temperature

and of *Kamimura et al.*[9] and *Hirakawa*[7] on single crystals gave *Curie* temperatures for Fe_7Se_8 of 423 K and 455 K, and 449 K and 443 K, resp.; *Hirone* and *Chiba*[3] and *Okazaki*[22] reported values of 447 K and 460 K, resp. The complicated change of magnetization with temperature in the range $0.16 \leqslant x \leqslant 0.24$ (54.3 to 56.8 at % Se) points to a superposition of two ferrimagnetic components with different *Curie* temperatures (Fig. 3). Measurements in the paramagnetic range[1] have also indicated the existence of a two-phase field ($\gamma + \beta$) between hexagonal γ-$Fe_{1-x}Se$ and monoclinic β-$Fe_{1-x}Se$. The inflection points of the magnetization curves of $Fe_{0.80}Se$ and $Fe_{0.79}Se$ (55.5 and 56.0 at % Se, resp.) at ~ 350 K (Fig. 3) are caused by the *Curie* temperature of the β-phase. The complete disappearence of magnetization at 426 K which is especially noticeable for $Fe_{0.80}Se$ with its higher γ-phase content corresponds to the *Curie* point of the hexagonal γ-phase.

The monoclinic alloys in the range $0.24 \leqslant x \leqslant 0.36$ (56.8 to ≈61 at % Se) are without exception ferrimagnetic with *Curie* points partly below room temperature. In Fe_3Se_4 (57.17 at % Se) the ferri—to paramagnetic transformation was found at 335 K, in good agreement with the value of 338 K obtained by measurements in the paramagnetic range[1]. In comparison *Hirone et al.*[2] and *Serre et al.*[4] reported 303 K and 320 K, resp. In the alloys with higher Se-contents, i.e. $Fe_{0.73}Se$, $Fe_{0.71}Se$, and $Fe_{0.69}Se$ (58.0, 58.5, and 59.1 at % Se, resp.), the transition to ferrimagnetic behaviour takes place at 246 K, 225 K, and 145 K, resp.

Table 2. *Experimental and theoretical saturation magnetization of ferrimagnetic iron selenides with* NiAs *structure*

Composition (at % Se)	Experimental magnetization		Theoretical magnetization	
	present results	literature[a]	model	neutron diffraction
52.80 $Fe_{0.89}Se$	5.2	≈ 5.6[2], 10.9[7] 13.5[9], 8.0[10]	9.2	
53.35 $Fe_{0.87}Se$	11.8		10.9	9.8[12]
54.02 $Fe_{0.85}Se$	11.4		13.1	
55.51 $Fe_{0.80}Se$	13.7		26.5	
56.01 $Fe_{0.79}Se$	13.8	≈ 3.0[2], ≈ 14.0[5] 12.0[7], 10.4[15]	32.6	
57.17 $Fe_{0.75}Se$	16.8		46.5	7.9[14], 7.3[15], 19.1[17]
57.97 $Fe_{0.73}Se$	13.4		56.1	
58.53 $Fe_{0.71}Se$	11.7		62.7	
59.06 $Fe_{0.69}Se$	(6.0)		69.0	

[a] In part these data refer to different temperatures, and in most cases had to be changed from emu/cm³ to emu/g. The necessary densities were taken from *Hägg* and *Kindström*[31]. Own values were obtained by extrapolation of T → 0 K.

The saturation magnetizations are listed in Table 2 and are plotted in Fig. 5 as a function of composition. Also listed are the results of other authors obtained with powders[2,5,15] and with single crystals[7,9,10]. In the hexagonal ferrimagnetic range $0.10 \leqslant x \leqslant 0.16$ (52.5 to 54.3 at % Se) the saturation magnetization increases rapidly to the maximum value of 11.8 emu/g for Fe_7Se_8 (3 *c*-type). The magnetization of the two-phase specimens $Fe_{0.80}Se$ and $Fe_{0.79}Se$ (55.5 and 56.0 at % Se, resp.) is determined by the respective ratio of the amounts γ/β. The magnetization of the monoclinic alloys $0.24 \leqslant x \leqslant 0.36$ (56.8 to 61.0 at % Se) decreases again starting at 16.8 emu/g for Fe_3Se_4 with increasing Se-content. A somewhat similar concentration dependence but slightly shifted in composition and with considerably lower values of magnetization was reported by *Hirone et al*[2]. Their magnetizations for Fe_7Se_8 and Fe_3Se_4 of 5.6 and 3.0 emu/g, resp., deviate strongly from the values of the present investigation. Measurements of *Hirakawa*[7] on single crystals of Fe_7Se_8 and Fe_3Se_4 at ≈ 100 K gave as results 10.9 and 12.0 emu/g, resp., *Kamimura et al.*[9] obtained with Fe_7Se_8 single crystals at 4.2 K a magnetization of 13.5 emu/g. From the data of *Adachi*[10] for Fe_7Se_8 a value of 8.0 emu/g was calculated. For Fe_3Se_4 powder *Kerimov et al.*[5] and *Lambert-Andron* and *Berodias*[15] reported a magnetization of ≈ 14 and 10.4 emu/g, resp.

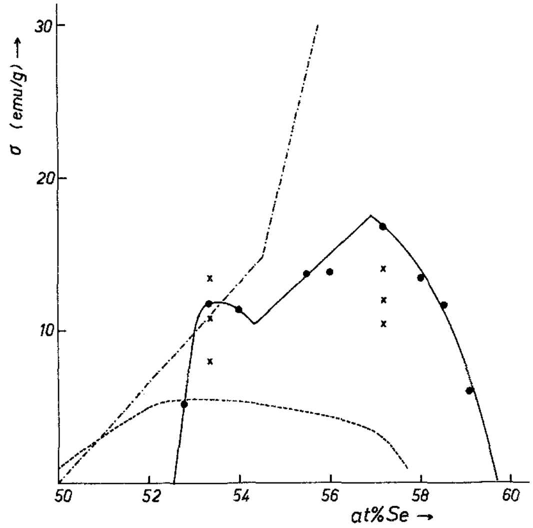

Fig. 5. Saturation magnetization of iron selenides with NiAs-structure as function of concentration (● present results, -·-·- calculated by ionic model, ---- *Hirone et al.*[2], x other authors[5,7,9,10,15])

The saturation magnetization can be treated theoretically by an ionic model in which the manner of distribution of Fe^{2+} and Fe^{3+} ions, and of iron vacancies (□) over the metal ion lattice plays a significant role. *Bertaut*[32] constructed several ionic models for Fe_7Se_8 based on different distributions of ions and vacancies which later on were applied by *Lotgering*[25] to nonstoichiometric iron sulfides. The best agreement with the experimental values for iron selenides could be obtained with the following already generally applied model. Due to considerations of valency the amounts of iron vacancies, Fe^{3+} and Fe^{2+} ions in $Fe_{1-x}Se$ are x, $2x$, and $1\text{-}3x$, resp. Since subtraction of iron ions takes place only in every other layer of the metal ion lattice perpendicular to the c-axis, one can divide the metal ion lattice in a completely filled sublattice A and in a partially filled sublattice B. The Fe^{3+} ions, if not present in large numbers ($0 \leqslant x \leqslant 1/6$), are supposed to be only in sublattice B which at $x = 1/6$ will be exclusively occupied by Fe^{3+} ions and iron vacancies. Additional Fe^{3+} ions from $x > 1/6$ onward will go into sublattice A until at $x = 1/3$ (Fe_2Se_3) occupancy will be complete. Under the assumption that the magnetizations of the sublattices have opposite directions the distributions

$$[Fe^{2+}_{0.5}]_A[Fe^{2+}_{0.5-3x}Fe^{3+}_{2x}\square_x]_B Se^{2-} \text{ for } 0 \leqslant x \leqslant 1/6 \tag{1 a}$$

$$[Fe^{2+}_{1-3x}Fe^{3+}_{3x-0.5}]_A[Fe^{3+}_{0.5-x}\square_x]_B Se^{2-} \text{ for } 1/6 \leqslant x \leqslant 1/3 \tag{1 b}$$

will allow the calculation of the average magnetic moment of an iron atom (μ) and the net magnetization ($\sigma = \sigma_A - \sigma_B$):

$$\mu = \frac{2x}{1\text{-}x}\mu_B;\ \sigma = \frac{2x}{1\text{-}x} Z\,\mu_B \text{ for } 0 \leqslant x \leqslant 1/6 \tag{2 a}$$

$$\mu = \frac{8x-1}{1-x}\mu_B;\ \sigma = \frac{8x-1}{1-x} Z\,\mu_B \text{ for } 1/6 \leqslant x \leqslant 1/3 \tag{2 b}$$

In Eqs. (2) Z is the number of iron atoms in 1 g alloy and μ_B the *Bohr* magneton. For the calculations the magnetic moments of Fe^{2+} and Fe^{3+} were assumed to be 4 μ_B and 5 μ_B, resp. In the monoclinic range no agreement was obtained between calculated and experimental values but for hexagonal alloys the experimental data are in approximate accord with the model (Table 2, Fig. 5). Much better results were obtained by calculating the saturation magnetization using magnetic moments obtained by neutron diffraction (Table 2). With the magnetic moments for Fe^{2+} and Fe^{3+} of 3.6 μ_B and 4.5 μ_B, resp., reported by *Andersen* and *Leciejewicz*[12] a saturation magnetization of 9.8 emu/g is calculated for Fe_7Se_8 which is only slightly below the experimental value of 11.8 emu/g. For Fe_3Se_4 results of *Andresen*[14], *Lambert-Andron* and *Berodias*[15], and *Andresen* and *Laar*[17] are available which give magnetizations of 7.9, 7.3, and 19.1 emu/g, resp. In comparison the experimental value for Fe_3Se_4 is 16.8 emu/g.

In conclusion it can be said that the proposed ionic model is sufficiently consistent with the para- and ferrimagnetic properties of the hexagonal NiAs-phase. However, its application to the monoclinically distorted NiAs-phase does not appear to be reasonable.

Acknowledgment

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