INFLUENCE OF THERMAL TREATMENT ON THE MAGNETIC PROPERTIES OF $NiFe_{2-x}Al_xO_4$

By L. Kozłowski

Laboratory of Solid State Physics, Institute of Metallurgy of the Academy of Mining and Metallurgy, Cracow*

And W. Zarek

Institute of Physics, Silesian University, Katowice**

(*Received February 15, 1972*)

The results of studies on the magnetic properties of ferromagnetic spinels $NiFe_{2-x}Al_xO_4$ in ferrimagnetic and paramagnetic region are given.

Strong influence of temperature and time of thermal treatment on the net magnetization and the temperature dependence of spontaneous magnetization is observed. Changes of magnetic properties due to thermal treatment are explained by changes in the cation distribution in the sublattices of the investigated spinel.

1. *Introduction*

The subject of the investigations were ferrimagnetic spinels called nickel aluminates-ferrites having the chemical formula $Ni\,Fe_{2-x}\,Al_xO_4$, where x denotes the number of Al^{3+} ions in the molecule and can vary from 0 to 2.

The magnetic properties of the investigated spinels depend mainly on the chemical composition of the sample, and for samples of given fixed composition they depend on the cation distribution in the A and B sublattices. According to Refs [1–3] the cation distribution in the sublattices can be presented by means of a simple notation:

$$(Ni_y^{2+}Al_b^{3+}Fe_{1-y-b}^{3+})\,[Ni_{1-y}^{2+}Al_{x-b}^{3+}Fe_{1-x+y+b}^{3+}]\,O_4^{2-} \tag{1}$$

where y and b are parameters determining the distribution of cations. The A and B sublattices are denoted by parentheses ( ), and square brackets [ ], respectively.

---

* Address: Zakład Fizyki Ciała Stałego, Instytut Metalurgii AGH, Kraków, Mickiewicza 30, Poland.

** Address: Instytut Fizyki, Uniwersytet Śląski, Katowice, Uniwersytecka 4, Poland.

Detailed studies [4] have shown that the cation distribution in the $NiFe_{2-x}Al_xO_4$ is significantly dependent on the temperature and the time of thermal treatment.

Annealing at temperatures higher than 400°C of samples cooled slowly from 1350°C to room temperature gives rise to the diffusion of Al^{3+} cations from *B* sites to *A* sites and simultaneous diffusion of Fe^{3+} cations in opposite direction.

For samples with $x > 1.00$ the annealing process gives also rise to the diffusion of Ni^{2+} cations to *A*-sites and simultaneous diffusion of Fe^{3+} cations to *B*-sites. As a result the number of Al^{3+} and Ni^{2+} cations occupying *A*-sites increases with increasing annealing temperature.

The proces of annealing of samples quenched previously from high temperature, at temperatures lower than the quenching temperature changes the direction of the migration of cations. In such a case the Al^{3+} and Ni^{2+} cations move from the *A* to the *B* sites thus shifting the Fe^{3+} cations to *A* sites.

The distribution of cations, both in slowly cooled samples and those quenched from high temperature, depends on the time of heating at constant temperature. During the heating process this distribution is subject to changes, tending to thermal equilibrium which corresponds to the temperature of thermal treatment.

The changes in the distribution of cations result in changes in the magnetic properties of the ferrite, in particular changes in the net megnetization, the Curie and the compensation temperature.

The present paper summarizes the results of investigations of the magnetic properties for nickel ferrite-aluminates in the ferrimagnetic and paramagnetic regions.

Special attention is paid to the influence of thermal treatment on the magnetic properties of the investigated spinels, in particular, on the net magnetization and the temperature dependence of spontaneous magnetization.

2. *Preparation of* $NiFe_{2-x}Al_xO_4$ *and thermal treatment of samples during final sintering process*

The samples were prepared using the standard ceramical method. Preliminary sintering occurred at 1000°C while the final sintering process at 1350°C. The time of final sintering depended on the contents of Al^{3+} ions in $NiFe_{2-x}Al_xO_4$. The sintering times were the greater, the greater the x value and varied from 5 hours for $x < 0.4$ to 16 hours for $x = 2.00$. After final sintering the samples were cooled slowly from 1350°C to room temperature for about 350 hours according to a previously elaborated program.

Radiographic studies made for all samples have shown that only the spinel phase exists, while the results of chemical analysis proved that the chemical compositions were consistent with those desired.

In order to study the influence of thermal treatment on the magnetic properties of $NiFe_{2-x}Al_xO_4$ a part of the slowly cooled samples was quenched from temperatures ranging from 500°C to 1350°C. The cation distribution existing at high temperatures was thus frozen.

3. *Apparatus*

The magnetic properties of $NiFe_{2-x}Al_xO_4$ were studied using a modified Sucksmith magnetic balance [5]. The sensitivity of the balance was varied from $5 \cdot 10^5$ div/N to $15 \cdot 10^5$ div/N and depended on the magnetic properties of the investigated samples. The measurement of specific magnetization and the magnetic susceptibility were made from 77 K to 1000 K in magnetic fields up to 10^3 kA/m. The measurement error did not exceed 1%.

4. *Measuring methods*

The magnetic balance method was used for measurements of the specific magnetization and the magnetic susceptibility of the investigated spinels depending on the magnetic field strength and temperature.

The specific magnetization σ and the magnetic susceptibility χ have been calculated using the formula for the force acting on the sample in nonuniform field.

The saturation magnetization σ_n for various temperatures was determined by extrapolation of magnetization curves plotted in σ *vs* $\frac{1}{H}$ coordinates to $H = \infty$.

On the basis of these data it was possibile to plot the dependence $\sigma_n(T)$ and by extrapolation to $T = 0$ to determine the saturation magnetization at 0 K.

The spontaneous magnetization σ_s at a given temperature was determined by extrapolation to $H = 0$ of the magnetization isotherme plotted in σ *vs* H coordinates.

For temperatures close to the Curie point T_c and to the compensation temperature T_K The spontaneous magnetization was determined by means of the thermodynamic coefficients method of Bielov [6].

In accordance with Ref. [6] the dependence of the magnetization σ on the applied magnetic field H is

$$a + c\sigma^2 = H/\sigma, \tag{2}$$

where a and c are thermodynamical coefficients. By plotting the dependence $\frac{H}{\sigma}(\sigma^2)$ for temperatures close to T_c or T_K and extrapolation to $\frac{H}{\sigma} = 0$ it was possible to determine spontaneous magnetization.

The Curie point and the compensation temperature were also determined by means of the thermodynamical coefficients method.

As it can be seen from Eq. (2) the dependence $\frac{H}{\sigma}(\sigma^2)$ in the vicinity of T_c and T_K is presented by a straight line whose intercept is the coefficient a and the slope equal to c. The value of a changes linearly with temperature and tends to zero when $T \to T_c$ or $T \to T_K$. The intercept of the graph of $a(T)$ with the temperature axis determines the Curie point or the compensation temperature. This method permits the Curie and the compensation temperature to be determined with the accuracy of ± 1 K.

The cation distribution in the sublattices of the spinel has been determined using the magnetic method elaborated by Smart [1] and Gorter [2]. In the case of $NiFe_{2-x}Al_xO_4$ this method consists in the solution of a system of equations

$$\sigma_0 = 3,7y+10b-5x+2,3, \tag{3}$$

$$\sigma_0/g_{eff} = 3y+5b-2,5x+1, \tag{4}$$

where σ_0 is the net magnetization, and g_{eff} the effective Landé factor.

The above method was used to determine the parameters y and b with the accuracy of $\pm 2.10^{-3}$ for samples with $1.00 < x < 1.75$.

For samples having $x < 1.00$ a simplified method of cation distribution was used. In accordance with Refs [1] and [2] it was accepted that the Ni^{2+} cations occupy the B sites only ($y = 0$). The cation distribution is then defined by a single parameter

$$b = \frac{\sigma_0 + 5x - 2,3}{10}, \tag{5}$$

which is determined directly from the measurements of net magnetization of the sample. The accuracy of the determination of the parameter b for $0 < x < 1$ amounted to $\pm 5 \cdot 10^{-4}$.

5. Results and interpretation of the relationships

Changes in the net magnetization σ_0 of nickel ferrite-aluminates are illustrated in Fig. 1. It was found that the net magnetization of both slowly cooled and quenched samples decreases with increasing Al^{3+} contents.

The decrease in net magnetization with increasing x is the result of the replacement of magnetic iron ions in nickel ferrite by nonmagnetic aluminium ions. For slowly cooled samples the net magnetization crosses the compensation point at $x \approx 0.70$ and $x \approx 1.60$. At this point the magnetic moments of both sublattices cancel, being equal and antiparallel, and thus the net magnetization of the sample is zero.

For $x < 0.70$ and $x > 1.60$ the magnetic moment σ_B of the sublattice B is greater than the magnetic moment σ_A of the sublattice B, and the net magnetization σ_0 which is equal to the difference between the magnetic moments those of the B and A sublattices is positive.

For intermediate x values the magnetic moment of the sublattice A is greater than that of B and the net magnetization of the samples is negative.

In case of samples quenched from sintering temperature the net magnetization decreases with increasing x, however, it does not change its sign. This means that in the whole x-range the value of the magnetic moment of the B sublattice is greater than that of sublattice A. Calculations of the parameters of the cation distribution have shown that in the sublattice A of quenched samples there are more Al^{3+} and Ni^{2+} cations than in case of slowly-cooled samples. Analogous dependences of σ_0 on x for the investigated spinels have been observed by Gorter [2], Nicolas [3], Maxwell and Pickart [7].

Changes in the net magnetization occurring with changing quenching temperature are shown in Fig. 2.

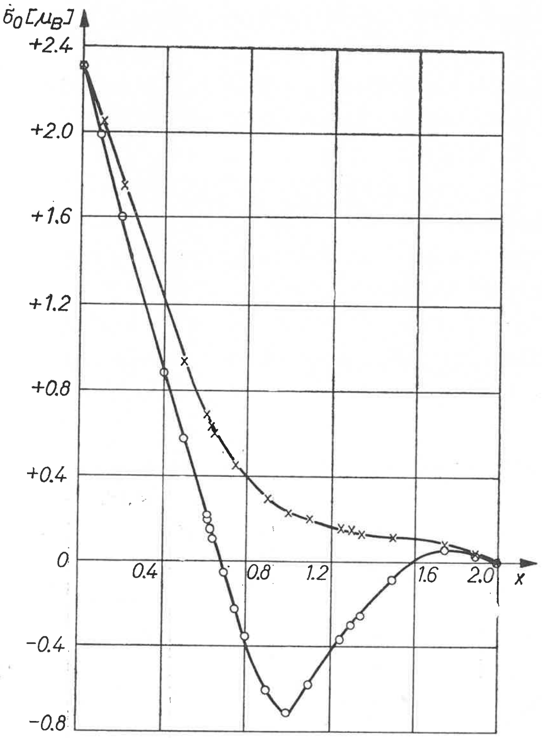

Fig. 1. Dependence of net magnetization σ_0 on the Al^{3+} ion contents in $NiFe_{2-x}Al_xO_4$. o–o–o — slowly-cooled samples, x—x—x — samples quenched from 1350°C

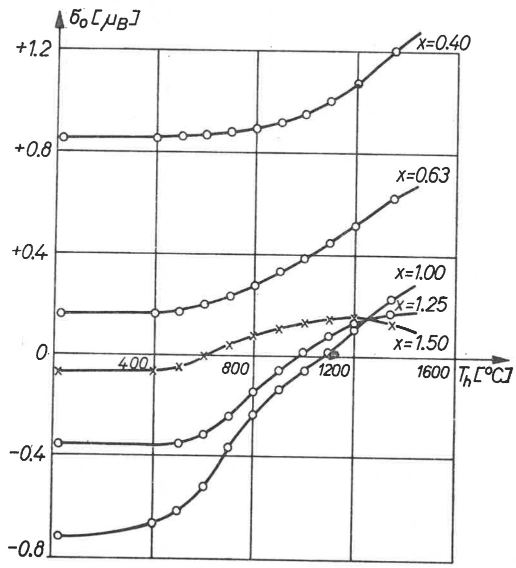

Fig. 2. Dependence of net magnetization of $NiFe_{2-x}Al_xO_4$ on quenching temperature

For slowly-cooled samples with positive net megnatization a systematic increase in the net magnetization with increasing temperature of thermal treatment has been observed. However, for slowly cooled samples with negative net magnetization the absolute value of this magnetization first decreases, becoming zero at a definite quenching temperature, and then increases with increasing quenching temperature.

Thus the study of the changes in the net magnetization with changing quenching temperature permit the determination of the sign of net manetization of $NiFe_{2-x}Al_xO_4$. Changes in the net magnetization with the temperature of thermal treatment are commonly connected with changes in cation distribution. It follows from the calculations of the cation distribution parameters that annealing of slowly-cooled samples gives rise to Al^{3+} cation transfer from the *B* to the *A* sites. The number of these cations in the sublattice

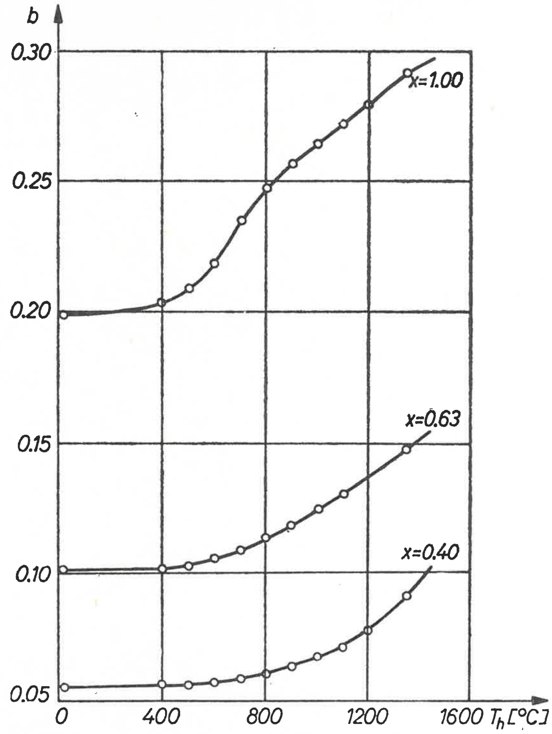

Fig. 3. Changes in the parameter *b* with quenching temperature

A increases, with increasing annealing temperature (Fig. 3). In the process of transfer to the *A* sites, the Al^{3+} cations shift the Fe^{3+} ions to the sublattice *B*.

In case of samples for which $x > 1.00$ the annealing process gives also rise to a transfer of Ni^{2+} ions to the *A* sites. This is also accompanied by a simultaneous transfer of Fe^{3+} ions to *B* sites.

As a result the number of Al^{3+} and Ni^{2+} ions accupying the *A*-sites increases with increasing temperature of thermal treatment (Fig. 4), thus decreasing the magnetic moment of the sublattice A. At the some time the increasing number of the magnetic Fe^{3+} ions in the B-sublattice results in its increasing magnetic moment.

The Curie point of slowly-cooled samples and those quenched from sintering temperature decreases monotonically from 853 K with increasing Al^{3+} ion contents. The changes

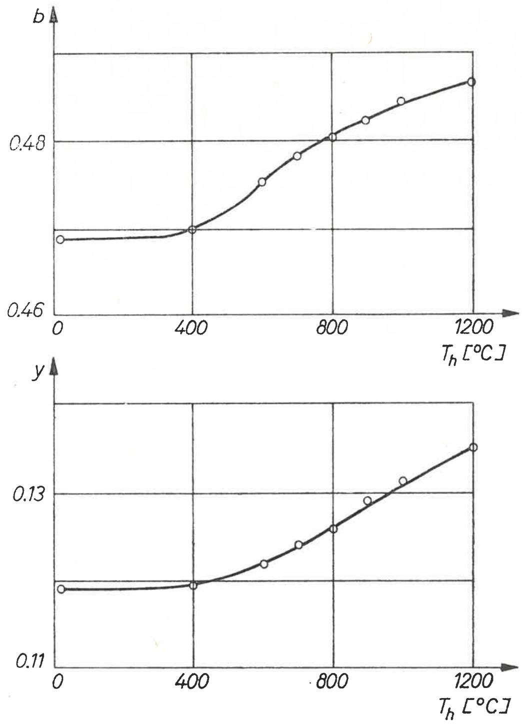

Fig. 4. Changes in the parameters y and b with quenching temperature for a sample with $x = 1.50$

in the Curie temperature occurring with the chemical composition of the sample are shown in Fig. 5.

The decrease in the Curie temperature with increasing x is also due to the replacement of Fe^{3+}-cations in nickel ferrite by nonmagnetic Al^{3+} ions. The increase in x is accompanied by decreasing exchange interaction between the sublattices A and B which defines the Curie point.

The slightly higher temperatures of the Curie point observed in case of quenched sample compared to those subjected to slow cooling can be explained by different cation distributions in both types of samples.

The temperature dependences of spontaneous magnetization σ_s observed for the majority of slowly cooled samples are similar to analogous dependences in ferromagnetics. Temperature dependences characterized by compensation points have been observed only in case of slowly cooled samples with $0.69 < x < 0.75$. An anomalous temperature dependence of spontaneous magnetization has been observed in a sample with $x = 1.50$.

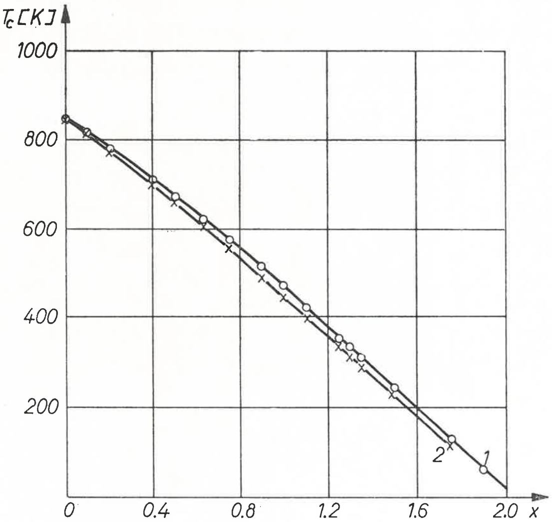

Fig. 5. Changes in the Curie temperature with the chemical composition of the sample; curve *1* — for slowly cooled sample, curve *2* — for sample quenched from 1350°C

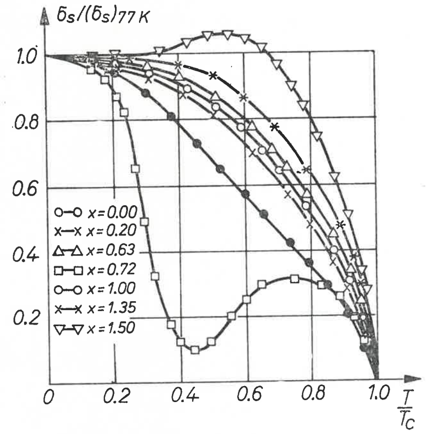

Fig. 6. Dependence of reduced spontaneous magnetization on reduced temperature for some slowly cooled $NiFe_{2-x}Al_xO_4$ samples

Fig. 6 shows the dependence of reduced spontaneous magnetization on reduced temperature for several slowly-cooled samples.

The shape the temperature dependence of spontaneous magnetization of $NiFe_{2-x}Al_xO_4$ is to a high extent dependent on thermal treatment.

This is particularly evident in case of samples with $x > 0.70$. The influence of thermal treatment is illustrated in Fig. 7.

No such influence, however, was observed in case of samples with $0 < x < 0.5$.

Detailed studies have shown that anomalous temperature dependence of spontaneous magnetization are only observed in such samples for which $|\sigma_s| < 0.1\ \mu_B$ at 77 K.

The compensation point appears only then when $\sigma_A > \sigma_B$ and $|\sigma_s| < 0.06\,\mu_B$ at 77 K. The condition at which the compensation point occurs can be reached by subjecting the sample to thermal treatment.

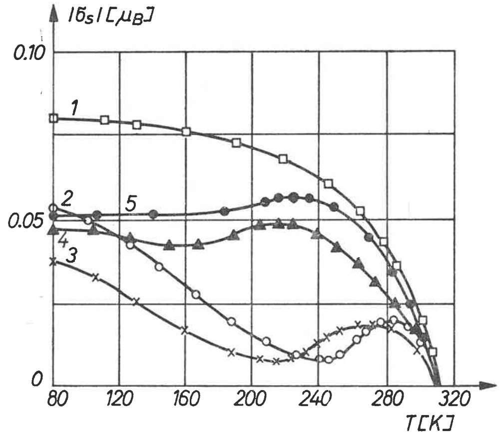

Fig. 7. Temperature dependences of spontaneous magnetization for a sample with $x = 1.35$ quenched from 1300°C (curve *1*) and annealed at 700°C for 1 minute (curve *2*), 5 minutes (curve *3*), 8 minutes (curve *4*)

It can be seen from Figs 6 and 7 that at the compensation point there occurs no total compensation of the magnetic moments of the sublattices *A* and *B*. At this point spontaneous magnetization becomes only a distinct minimum.

Incomplete compensation was explained by the existence in the sample of small microregions which slightly differ in the compensation points [8].

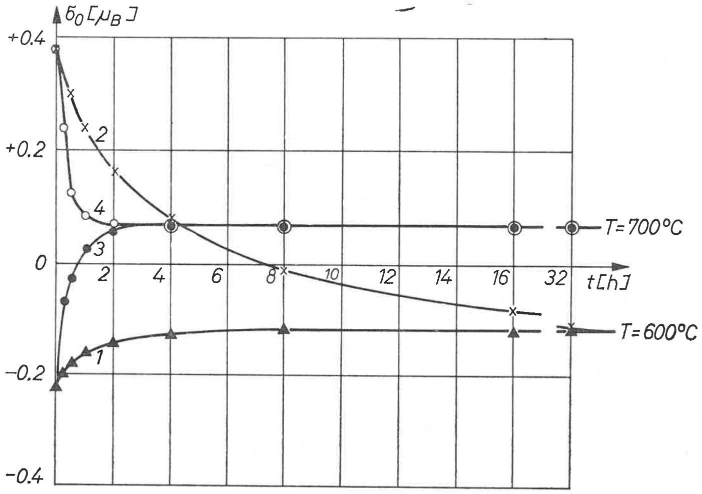

Fig. 8. Changes in net magnetization with annealing time for a sample with $x = 0.75$; curves *1* and *3*: slowly-cooled sample annealed at the temperatures 600 and 700°C, rescpectively; curve *2* and *4*: a sample quenched from 1200°C and annealed at the temperatures 600 and 700°C, respectively

In addition to the observation of compensation points in the temperature dependence of spontaneous magnetization and in changes of net magnetization with chemical composition and temperature of thermal treatment, the compensation effect has also been observed in changes of net magnetization occurring with changing time of annealing at constant temperature.

Fig. 8 shows an example of changes in net magnetization σ_0 with annealing time for slowly-cooled samples with $x = 0.75$ annealed at 600° and 700°C and for samples quenched from 1200°C and those annealed at temperatures 600° and 700°C.

The slowly cooled sample which was later annealed at 600°C did not exhibit any compensation point in the dependence of net magnetization σ_0 on annealing time t similarly as the sample quenched from 1200°C and annealed at 700°C.

The compensation point in the $\sigma_0(t)$ dependence occurs only then when the signs of net magnetization of the sample before and after establishing thermal equilibrium of the cation distribution at the given temperature point are opposite.

It was found that the compensation points in nickel ferrite-aluminates appear as functions of the above variables only for compositions with $0.7 < x < 1.50$.

In the paramagnetic region the nickel ferrite-aluminates exhibit hyperbolic dependence of reciprocal susceptibility on temperature, which is typical for ferrimagnetics. The dependence $1/\chi(T)$ for $NiFe_{2-x}Al_xO_4$ is described by

$$1/\chi = T/C + 1/\chi_0 - \delta/T - \theta, \tag{7}$$

where $\frac{1}{\chi_0}$, δ, and θ are parameters of the equation of the hyperbola which are connected with cation distribution and molecular field coefficients, and C is the Curie constant of the sample.

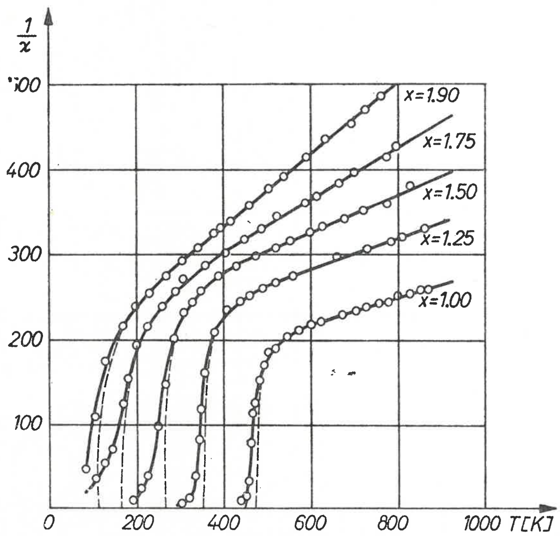

Fig. 9. Temperature dependences of magnetic susceptibility of $NiFe_{2-x}Al_xO_4$

Fig. 9 shows the temperature dependence of reciprocal molar susceptibility for several slowly-cooled samples.

The parameters of the equation of the hyperbola have been determined from the experimental $\frac{1}{\chi}(T)$ dependences by means of the Aleonard method [9]. Using the obtained values of $\frac{1}{\chi_0}$ δ, C, and θ it was possible to calculate the theoretical $\frac{1}{\chi}(T)$ dependences. The latter are shown in Fig. 9 by dashed lines. Similar $\frac{1}{\chi}(T)$ dependences have been obtained for samples quenched from 1200°C.

6. *Conclusions*

As a result of the studies made in the piesent work it was found:

1. The net magnetization of slowly cooled samples decreases with increasing contents of Al^{3+} ions in $NiFe_{2-x}Al_xO_4$. At $x \approx 0.70$ and $x \approx 1.60$ the magnetic moments of the sublattices A and B compensate (Fig. 1).

2. The net magnetization of samples quenched from sintering temperature also decreases with increasing x, but does not reach compensation point (Fig. 1).

3. The value of net magnetization of $NiFe_{2-x}Al_xO_4$ depends distinctly on the temperature and time of thermal treatment (Figs 2 and 8).

4. The studies of changes in net magnetization with thermal treatment temperature permit the determination which sublattice has the dominant magnetic moment.

5. Changes in net magnetization occurring during thermal treatment result from changes in cation distribution (Figs 3 and 4).

6. The temperature of the Curie point of slowly-cooled samples and those quenched from sintering temperature decreases monotonically with increasing Al^{3+} ion contents in the investigated spinel (Fig. 5). The Curie temperature of quenched samples is slightly lower than that of cooled slowly.

7. The shape of the temperature dependence of spontaneous magnetization depends on the chemical composition and chemical treatment of the sample (Figs 6 and 7).

8. In the paramagnetic region the character of the dependence of reciprocal susceptibility on temperature for the investigated spinels is hyperbolic.

9. Systematic investigations of the influence of thermal treatment on the magnetic properties of compounds with spinel structure can provide information on the cation distribution in the sublattices and the kinetics of cation transfer in the spinel lattice. The results of the study of the kinetics of cation transfer in the spinel lattice of $NiFe_{2-x}Al_xO_4$ will be presented in another paper.

REFERENCES

[1] J. S. Smart, *Phys. Rev.*, **94**, 847 (1954).
[2] E. W. Gorter, *Philips Res. Rep.*, **9**, 295 (1954).
[3] J. Nicolas, *J. Phys. Chem. Solids*, **28**, 847 (1967).

[4] L. Kozłowski, W. Zarek, *Acta Phys. Polon.*, (in press).
[5] Z. Obuszko, *Acta Phys. Polon.*, **24**, 135 (1963).
[6] K. P. Belov, *Magnitnye prevrashchenya*, Moskva 1959.
[7] L. Maxwell, J. S. Pickart, *Phys. Rev.*, **92**, 1120 (1953).
[8] K. P. Belov, K. M. Bolshova, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **28**, 1282 (1958).
[9] R. Aleonard, *J. Phys. Chem. Solids*, **15**, 197 (1960).