A MAGNETIC METHOD OF THE STUDIES ON THE KINETICS OF CATION TRANSFER IN THE NiFe$_{2-x}$Al$_x$O$_4$ LATTICE

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Detailed studies of the influence of thermal treatment on cation distribution in the sublattices A and B have been made for some selected compositions of the NiFe$_{2-x}$Al$_x$O$_4$ spinel. Slowly cooled samples and those quenched from 1200°C were annealed at 600°C, 700°C, and 800°C for different times. After each annealing the samples were quenched in ice-water mixture. Changes in cation distribution were followed by measuring net magnetization and the effective Lande g-factor. On the basis of the investigation of the process of the approach of the cation distribution to thermal equilibrium state at different temperatures the time constants and the jumping frequencies of jumps of Al^{3+} and Ni^{2+} cations respectively, from the A to the B sites with the simultaneous transfer of the Fe^{3+} ions to the A sites. From considerations on the cation distribution in thermal equilibrium it was possible to calculate the energies W_1 and W_2 which are equal to the differences between the potential energy before and after mutual interchange of Al^{3+} and Fe^{3+} with Ni^{2+} and Fe^{3+}.

1. Introduction

The results of the studies on the influence of thermal treatment on the magnetic properties of the NiFe$_{2-x}$Al$_x$O$_4$ spinel have shown that the cation distribution in the sublattices distinctly depends on thermal treatment.

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The present paper concerns the kinetics of cation transfer in the $NiFe_{2-x}Al_xO_4$ spinel lattice and the determination of the activation energies which are characteristic for these processes.

The change of a site in the spinel lattice requires a sufficient amount of energy to be supplied to the cation. This energy is provided by the thermal vibration of the ionic lattice.

The energy is used by the migrating cations to force the potential barrier which separates its site from that to which it is transferred (for drawing aside and forcing the way through the anions) and for forcing of the differences in the potential energies which exists between these sites (different coordinations of anions forming the B and the A sites).

The total energy which is necessary for the cation to be transferred from the B site to the A site is equal to the sum of both these energies.

It follows from Refs [2–5] that annealing the ferrite at sufficiently high temperature give rise to the tansfer of cations from one type of sites to the other, during which process the transfer of one type of cation from an A site to a B site is accompanied by the transfer of another type of cation in opposite direction and *vice versa*. Thus the problem of interchange of positions in the spinel lattice by two types of ions and consequently by process of thermal treatment can be regarded as a diffusion process. This process is characterized by two activation energies (Fig. 1); E — which is the height of the potential barrier which
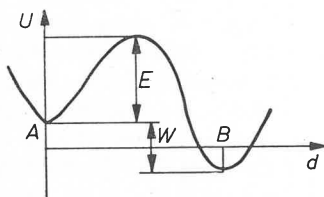

Fig. 1. Schematic dependence of binding energy on the distance between the sublattices A and B

separates the two adjacent sites, and W — which is the difference between the potential energies before and after the interchange of the sites by the two cations. Both activation energies can be determined among others from studies on the approach of the cation distribution to its equilibrium state [6].

The studies on the influence of thermal treatment on the distribution of cations in $NiFe_{2-x}Al_xO_4$ were restricted to compositions in the range between $0 < x < 0.75$ [6]. In this composition range one can assume that only the Al^{3+} and Fe^{3+} ions participate in this process interchanging their sites. The studies on the diffusion processes for $x > 1.00$ are complicated by the specific properties of the Ni^{2+} ions which also participate in this process.

The present paper gives the results of the studies on the influence of thermal treatment on cation distribution in $NiFe_{2-x}Al_xO_4$ for a wide composition range. In order to calculate the activation energy which characterizes the processes of cation transfer in $NiFe_{2-x}Al_xO_4$ we have made use of the considerations of Nicolas [6]. These considerations have been extended for the case in which also Ni^{2+} cations participate.

2. Experimental procedure of the determination of activation energies which characterize the diffusion process in $NiFe_{2-x}Al_xO_4$

The activation energy E_1 which is necessary to bring an Al^{3+} cation from the A to the B site (with a simultaneous transfer of an Fe^{3+} cation in opposite direction) and the activation energy E_2 which necessary to transfer a Ni^{2+} cation from A to B (with a simultaneous transfer of Fe^{3+} from B to A) have been determined on the basis of studies of the approach of the cation distribution to thermal equilibrium.

The distribution cations in the spinel sublattices have been presented in the following notations:

$$(Ni_y^{2+}Al_b^{3+}Fe_{1-y-b}^{3+})[Ni_{1-y}^{2+}Al_{x-b}^{3+}Fe_{1-x+y+b}^{3+}]O_4^{2-}. \tag{1}$$
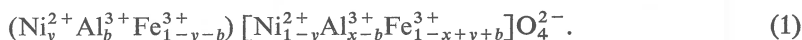
Cations in parentheses ( ) are those occupying the A sublattice while those in square brackets [ ] are in the B sublattice, and y and b are parameters describing the distribution of cations. In order to determine the above-mentioned activation energies the changes in the cation distribution parameters y and b occuring during the annealing times have been utilized. In accordance with Ref. [6] the process of the approach of cation distribution to the state of equilibrium in case when in the diffusion process only the Al^{3+} and Fe^{3+} participate is described by the differential equation:

$$dt = \frac{-db}{K_{21}(1-K)(b-b_1)(b-b_2)}, \tag{2}$$

where

$$K = \frac{K_{12}}{K_{21}} = \frac{b_1(1-x+b_1)}{(x-b_1)(1-b_1)} = \exp\left(\frac{-W_1}{kT}\right) \tag{3}$$

is the equilibrium constant.

K_{12} is the jumping frequency of Al^{3+} cations from the B to the A sites, K_{21} is the jumping frequency of Al^{3+} cations from the A to the B sites, W_1 is the energy characterizing the difference of the potential energies before and after the interchange of the Al^{3+} and Fe^{3+} ions, and b_1 and b_2 are the roots of the denominator of Eq. (2), b_1 being the parameter of the distribution of cations in thermal equilibrium, and

$$b_2 = \frac{-Kx}{b_1(1-K)}. \tag{4}$$

After integrating Eq. (2) from 0 to t and correspondingly from b_0 to b one obtains

$$Z = \frac{(b-b_1)(b_0-b_2)}{(b-b_2)(b_0-b_1)} = \exp\left(\frac{-t}{\tau}\right), \tag{5}$$

where

$$\tau = \frac{1}{(b-b_1)(1-K)K_{21}} \tag{6}$$

is the time constant characterizing the approach of the cation distribution to thermal equilibrium.

Making use of the experimental data concerning the changes of the parameter b with time of annealing at constant temperature we have determined the time constants of the approach of cation distribution to thermal equilibrium and the jumping frequency for jumps of Al^{3+} ions from A to B sites and *vice versa*.

The knowledge of the jumping frequencies K_{21} and K_{12} for several temperatures permitted the determination of activation energies E_1 and $(E_1 + W_1)$

$$K_{21} = f_0 \exp\left(\frac{-E_1}{kT}\right) \tag{7}$$

$$K_{12} = f_0 \exp\left(-\frac{E_1 + W_1}{kT}\right) \tag{8}$$

where f_0 is the normalization constant and k the Boltzmann constant.

In the present paper the considerations of Nicolas have been applied to the case in which also the Ni^{2+} ions participate. It was assumed that the diffusion of Al^{3+} and Ni^{2+} ions in one direction is always accompanied by the diffusion of Fe^{3+} cations in the opposite direction. The number of the migrating Fe^{3+} cations is equal to the sum of Al^{3+} and Ni^{2+} cations. The process of action transfer has been separated into two simultaneous processes:

I) process of the interchange of Al^{3+} and Fe^{3+} cations characterized by the activation energies E_1 and W_1,

II) process of interchange on Ni^{2+} and Fe^{3+} ions characterized by the activation energies E_2 and W_2.

In this case the approach of the cation distribution to thermal equilibrium state is described by two differential equations:

$$dt = \frac{-db}{K_{21}(1-K)(b-b_1)(b-b_2)} \tag{9}$$

$$dt = \frac{-dy}{K'_{21}(1-K')(y-y_1)(y-y_2)}, \tag{10}$$

where

$$K = \frac{K_{12}}{K_{21}} = \frac{[n(1-x)+b_1]b_1}{(n-b_1)(x-b_1)} = \exp\left(\frac{-W_1}{kT}\right), \tag{11}$$

$$K' = \frac{K'_{12}}{K'_{21}} = \frac{[m(1-x)+y_1]y_1}{(m-y_1)(1-y_1)} = \exp\left(\frac{-W_2}{kT}\right), \tag{12}$$

are the equilibrium constants for the processes I and II, respectively.

K_{12} and K_{21} are the jumping frequencies of Al^{3+} cations from the B to the A sites and from A to B, respectively, while K'_{12} and K'_{21} are the corresponding jumping frequencies of the Ni^{2+} ions.

The coefficients b_1 and y_1 are parameters describing the equilibrium distribution of cations while

$$b_2 = \frac{-Knx}{b_1(1-K)}, \tag{13}$$

$$y_2 = \frac{-K'm}{y_1(1-K')}, \tag{14}$$

where

$$m/n = y_1/b_1. \tag{15}$$

After integration of Eqs (9) and (10) between 0 and t and correspondingly from b_0 to b and y_0 to y we have obtained

$$Z = \frac{(b-b_1)(b_0-b_2)}{(b-b_2)(b_0-b_1)} = \exp\left(\frac{-t}{\tau}\right), \tag{16}$$

$$Z_1 = \frac{(y-y_1)(y_0-y_2)}{(y-y_2)(y_0-y_1)} = \exp\left(\frac{-t}{\tau'}\right), \tag{17}$$

where

$$\tau = \frac{1}{(b_1-b_2)(1-K)K_{21}}, \tag{18}$$

$$\tau' = \frac{1}{(y_1-y_2)(1-K')K'_{21}}. \tag{19}$$

The manner in which the time constants τ and τ' are determined is the same as in the previously discussed case.

From these time constants the corresponding jumping frequencies Al^{3+} cations, have been determined as functions of the thermal treatment temperature. In accordance with Ref. [6] it was accepted that

$$K_{21} = f_0 \exp\left(\frac{-E_1}{kT}\right) \tag{20}$$

$$K_{12} = f_0 \exp\left(-\frac{E_1+W_1}{kT}\right) \tag{21}$$

and

$$K'_{21} = f'_0 \exp\left(\frac{-E_2}{kT}\right) \tag{22}$$

$$K'_{12} = f'_0 \exp\left(-\frac{E_2+W_2}{kT}\right). \tag{23}$$

Eqs (11) and (12) as well as (20)–(23) permit the determination of activation energies E_1, E_2, W_1 and W_2 which characterize the process of Al^{3+}, Ni^{2+} and Fe^{3+} cation transfer in the spinel lattice of $NiFe_{2-x}Al_xO_4$

3. Preparation of samples and thermal treatment

Detailed investigation of the influence of thermal treatment on cation distribution in $NiFe_{2-x}Al_xO_4$ has been performed in a series of samples with $x = 0.63$, 0.75, 1.00, 1.25, 1.35, and 1.50.

There choice of those samples with the above-mentioned compositions has been made on the basis of the results of studies of the magnetic properties of these samples [1].

The samples were prepared by means of the ceramical method. They were first sintered at 1000°C and finally at 1350°C. The final sintering time depeded on the Al^{3+} contents; it varied from 7 hours for $x = 0.63$ to 13 hours for $x = 1.50$.

After final sintering the samples were cooled slowly according to a previously elaborated program from 1350°C to room temperature for about 350 hours.

All samples were subject to X-ray diffraction investigation which showed the presence of spinel phase only. Quantitative chemical analysis confirmed that the compositions of the samples are in agreement with those desired.

In order to study the kinetics of cation transfer and to determine the activation energies, both the slowly cooled samples and those quenched from 1200°C were annealed:

at 600°C for 1/4, 1/2, 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, and 1024 hours

at 700°C and 800°C for 1/30, 1/16, 1/8, 1/4, 1, 2, 4, 8, 16, 32, and 64 hours.

After each annealing the samples were quenched in ice-water mixture to freeze the cation distribution which existed at the particular time. In addition, the slowly cooled samples were annealed at 900°C, 1000°C, 1100°C, and 1200°C. After two hours of annealing at a given temperature they were quenched in ice-water mixture.

Small size of samples used in the present experiment (diameter less than 1 mm) guaranteed immediate heating to the temperature desired and proper quenching.

4. Experimental procedure

The studies of the diffusion processes in $NiFe_{2-x}Al_xO_4$ were carried out by means of the magnetic method. The changes in the cation distribution were followed by measurement of the net magnetization σ_0 of the sample and the effective Laude factor g_{eff}. In accordance with Refs [1], [6], [7] and [8] the parameters of the cation distribution y and b (Eq. (1)) for $x > 1.00$ were determined from the set of equations

$$\sigma_0 = 3.7y + 10b - 5x + 2.3, \tag{24}$$

$$\sigma_0/g_{eff} = 3y + 5b - 2.5x + 1. \tag{25}$$

For $x < 1.00$ it was assumed that Ni^{2+} cations occupy the B sites only ($y = 0$) cf. Ref. [8]. The cation distribution is then defined by a single parameter

$$b = \frac{\sigma_0 + 5x - 2.3}{10},$$ (26)

which can be determined directly from measurements of net magnetization. The latter were carried out with the use of a modified Sucksmith balanse [9]. The error did not exceed 1%.

The precision of the determination of y and b was $\pm 2 \cdot 10^{-3}$ for $1.00 \leqslant x \leqslant 1.75$ and $5 \cdot 10^{-4}$ for $x < 1.00$.

5. Results of measurements and discussion

The influence of annealing time on net magnetization of the investigated samples is illustrated in Figs 2 and 3. Changes in net magnetization are first large and then become smaller during further annealing. After some definite annealing time which depends on
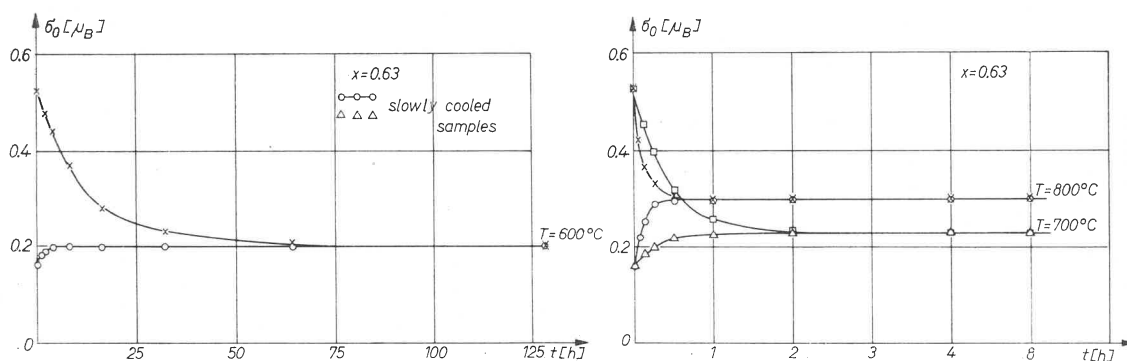

Fig. 2. Changes in net magnetization with annealing time for samples with $x = 0.63$

the temperature, the magnetization becomes constant and further annealing does not affect its value.

The magnitude of the changes in net magnetization which occur during the annealing process at constant temperature depends on the chemical composition of the sample and on the temperature. It was found that annealing at constant temperature of slowly-cooled samples and those quenched from 1200°C leads to identical values of stabilized net magnetization.

The changes in net magnetization observed during the annealing process result from changes in the distribution of cations. It was found that for $x < 1.00$ the process of annealing in case of slowly cooled samples gives rise to the diffusion of Al^{3+} ions from the B to the A sites with a simultaneous diffusion of Fe^{3+} ions from A to B sites. The number of Al^{3+} cations which occupy the A sublattice increases with increasing annealing time.

In case of slowly-cooled sample with $x > 1.00$ the annealing process gives rise, in

addition, to the diffusion of Ni^{2+} ions from the B to the A sites. Simultaneously the Fe^{3+} ions are transferred to the B sites. As a result for $x > 1.00$ the number of Ni^{2+} and Al^{3+} occupying the sublattice A increases.

Examples of changes in the parameters defining the cation distribution which occur during the annealing process are shown in Fig. 4 for $x < 1.00$ and Figs 5 and 6 for $x > 1.00$. After a certain annealing time, thermal equilibrium is established in the distribution of cations. This equilibrium depends on the annealing temperature.

During the process of annealing at the temperatures of 600°C, 700°C and 800°C of samples previously quenched from 1200°C, the Al^{3+} cations and also Ni^{2+} cations (for $x > 1.00$) return to the B sites and the Fe^{3+} cations to the A sites.

After a certain annealing time the state of equilibrium identical as that observed in case of slowly cooled samples is established.

The establishment of identical states of thermal equilibrium in both cases permits the kinetics of cation transfer to be studied in two ways:

a) annealing of slowly-cooled samples,

b) annealing of samples quenched from high temperature at temperatures lower than the quenching temperature.

From the dependences $b(t)$ and $y(t)$ determined it was possible to calculate the parameters b_0, b_1, b_2 and y_0, y_1, y_2. Making use of Eqs (5), (16) and (17) as well of (6), (18), and (19) we have determined the time constants for the approach of the cation distribution to thermal equilibrium and the jumping frequencies for the jump of Al^{3+} and Ni^{2+} ions from the A to the B sites and *vice versa*. The calculations of these quantities have been carried out for slowly cooled samples and for samples quenched from 1200°C annealed at 600, 700, and 800°C.

The values of the time constants and the jumping frequencies are listed in Table I for a sample with $x = 0.63$, and in Tables II and III for $x = 1.25$. The jumping frequencies have been determined with the accuracy of $\pm 3\%$.

From the data listed in Tables I–III it can be seen that the jumping frequencies of Ni^{2+} and Al^{3+} cations from A to be B sites are about one order of magnitude greater than

TABLE I

T [°C]	$10^{-2} \tau$ [sec]	$10^4 K_{21}$ [sec^{-1}]	$10^4 K_{12}$ [sec^{-1}]
600	359.6	0.46	0.04
700	17.7	7.60	0.80
800	2.3	55.000	6.70

TABLE II

T [°C]	$10^{-2} \tau$ [sec]	$10^4 K_{21}$ [sec^{-1}]	$10^4 K_{12}$ [sec^{-1}]
600	625.0	0.27	0.02
700	22.9	5.50	0.65
800	3.9	38.50	5.30

TABLE III

T [°C]	$10^{-2}\,\tau'$ [sec]	$10^4\,K_{21}'$ [sec^{-1}]	$10^4\,K_{12}$ [sec^{-1}]
600	1330.0	0.4	0.01
700	33.7	14.0	0.54
800	1.7	270.0	12.00

the jumping frequencies of these cations in opposite direction. This means that in $NiFe_{2-x}$ Al_xO_4 the Ni^{2+} and Al^{3+} are more frequently occupying the B sites than the A sites and thus shift the Fe^{3+} cations to the A sites. The jumping frequency of Ni^{2+} from the A to B sites which is greater than that of Al^{3+} ions indicates that the strongest individual tendency to occupy the B sites in the investigated spinel is exhibited by the Ni^{2+} cations. Thus the first to occupy the B sites in $NiFe_{2-x}Al_xO_4$ are the Ni^{2+} cations, then the Al^{3+} and the last the Fe^{3+} cations.

From the knowledge of the jumping frequencies we have calculated the activation energies E_1 and E_2 which are necessary for the transfer of Al^{3+} and Ni^{2+} cations from the A to the B sites with the simultaneous transfer of Fe^{3+} cations to the A sites. The calculation of these two energies have been carried out for both slowly-cooled samples and those

TABLE IV

x	E [eV]	E [eV]
0.63	1.9	—
0.75	1.8	—
1.00	1.9	—
1.25	2.0	2.4
1.35	2.0	2.2
1.50	1.8	1.9

quenched from 1200°C subjected to annealing at 600°, 700°C and 800°C. In both cases identical values have been obtained. The values of the activation energy for the investigated compositions are listed in Table IV.

The activation energies have been determined with the accuracy of ±0.3 eV.

Taking into account the errors in the determination of E_1 it is possible to assume that E_1 is constant (1.9±0.3) eV and does not depend on the chemical composition x of the sample.

It is not possible to make complete interpretation of changes in the activation energy E_2 with chemical composition since the number of investigated samples is too low. One may only expect that for $x < 1.00$ the values of E_2 are greater than for $x > 1.00$, and therefore in the former case the Ni^{2+} cations either do not change their sites or only a very limited number migrates to the A sites.

It was assumed that the mean value of E_2 amounts to (2.20±0.3) eV. This value is slightly higher than E_1 which suggests that the Ni^{2+} cation requires more energy to overcome the potential barrier between A and B than the Al^{3+} ion. Consequently the number

of Ni^{2+} cations which change their positions as a result of thermal treatment is smaller than the number of Al^{3+} cations.

The distribution of cations in thermal equilibrium state is characterized by the activation energies W_1 and W_2. The values of W_1 are listed in Table V for several temperatures. Table VI gives the values of W_2 for $x > 1.00$. The accuracy of both energies is ± 0.02 eV.

The comparison of Tables IV and V shows that the difference of the potential energies before and after the interchange of the positions of the cations Al^{3+} and Fe^{3+}, as well as

TABLE V

x	W_1 (eV)				
	$T = 006[°C]$	$T = 700\ [°C]$	$T = 800\ [°C]$	$T = 900\ [°C]$	$T = 1000\ [°C]$
0.63	0.17	0.18	0.19	0.20	0.21
0.75	0.17	0.18	0.19	0.20	0.21
1.00	0.18	0.19	0.20	0.21	0.23
1.25	0.17	0.18	0.19	—	—
1.35	0.17	0.18	—	0.21	—
1.50	0.18	0.18	0.19	0.20	0.21

TABLE VI

x	W_2 (eV)				
	$T = 600\ [°C]$	$T = 700\ [°C]$	$T = 800\ [°C]$	$T = 900\ [°C]$	$T = 1000\ [°C]$
1.25	0.27	0.28	0.29	—	0.32
1.35	0.27	0.28	—	0.31	—
1.50	—	0.28	0.30	0.31	0.34

Ni^{2+} and Fe^{3+} depends on the temperature of thermal treatment. Thus the energies W_1 and W_2 depend on the number of Al^{3+} and Ni^{2+} cations in A sites. Smaller W_1 and W_2 values correspond to the state in which the Al^{3+} and Ni^{2+} cations occupy the B sites.

6. Conclusions

The present analysis and the discussion of the results obtained allows us to make the following statements:

1. The process of transfer of Al^{3+}, Ni^{2+} and Fe^{3+} cations in the $NiFe_{2-x}Al_xO_4$ spinel lattice is characterized by the following activation energies,

a) the activation energies $E_1 = (1.9 \pm 0.3)$ eV and $(E_1 + W_1) = (2.1 \pm 0.3)$ eV which are connected with the interchange of Al^{3+} and Fe^{3+} cations;

b) the activation energies $E_2 = (2.2 \pm 0.3)$ eV and $E_2 + W_2 = (2.4 \pm 0.3)$ eV which are connected with the interchange of Ni^{2+} and Fe^{3+} cations.
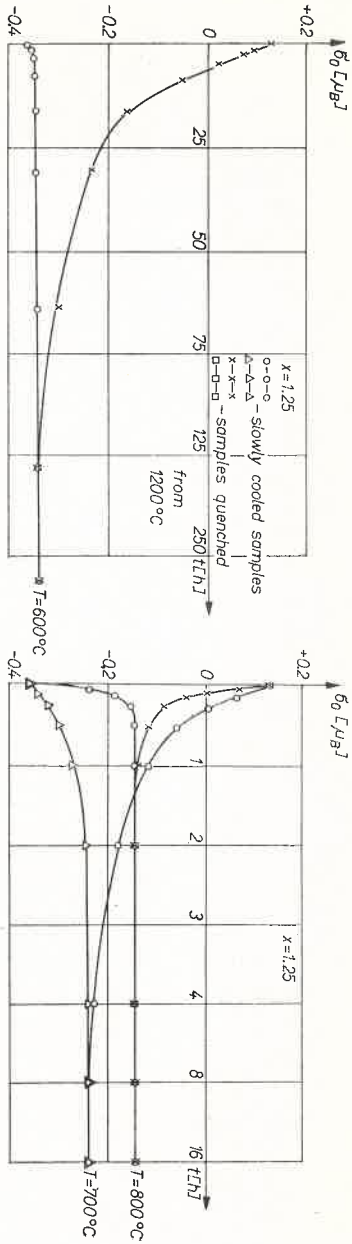
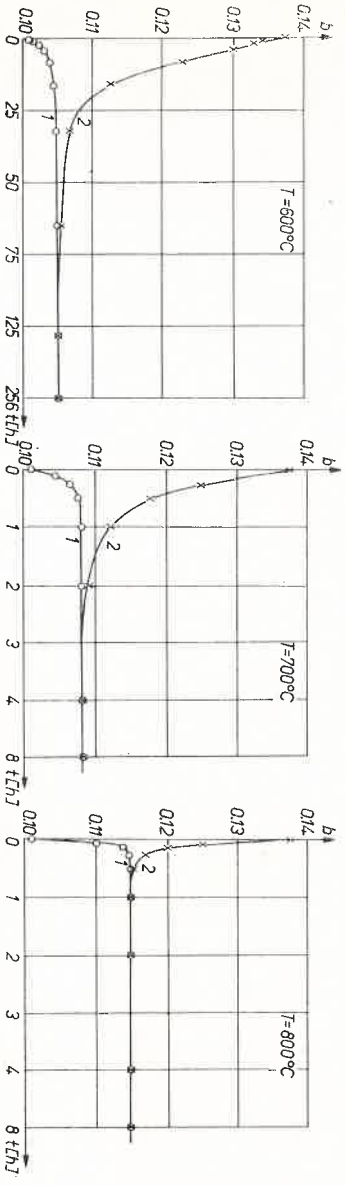Fig. 3. Changes in net magnetization with annealing time for samples with $x = 1.25$

Fig. 4. Changes in the cation distribution parameter b with annealing time for samples with $x = 0.63$; curve $1 - b(t)$ dependence for a slowly cooled sample annealed at 600, 700, and 800°C; curve $2 - b(t)$ dependence for a sample quenched from 1200°C and then annealed at 600, 700, and 800°C
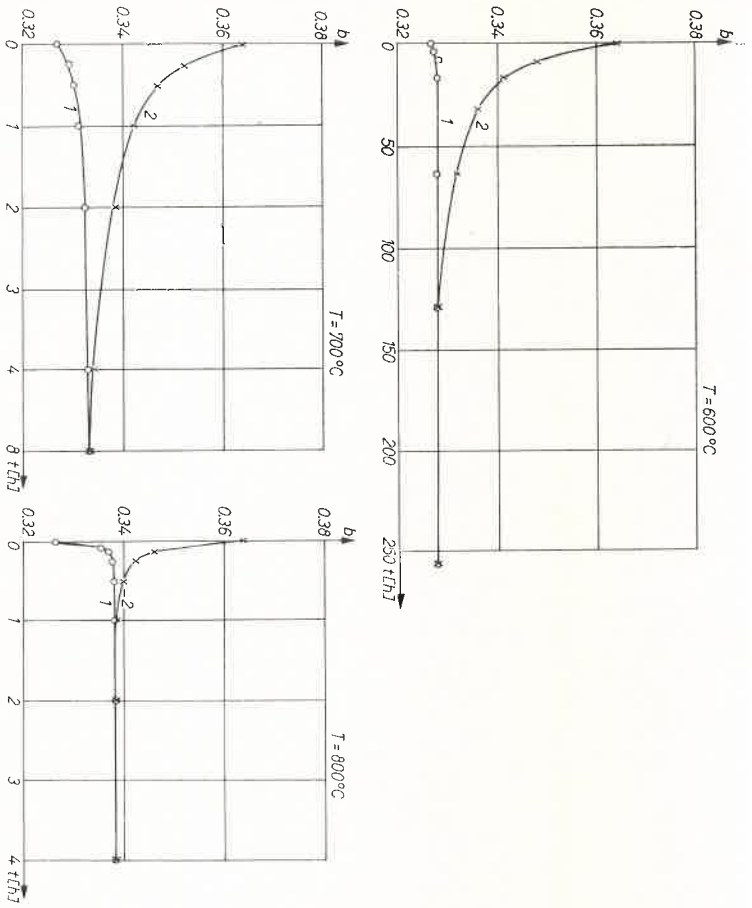
Fig. 5. Changes in the parameter b with annealing time for samples with $x = 1.25$; curve $1 - b(t)$ dependence for a slowly cooled sample annealed at 600, 700, and 800°C; curve $2 - b(t)$ dependence for a sample quenched from 1200°C and then annealed at 600, 700, and 800°C
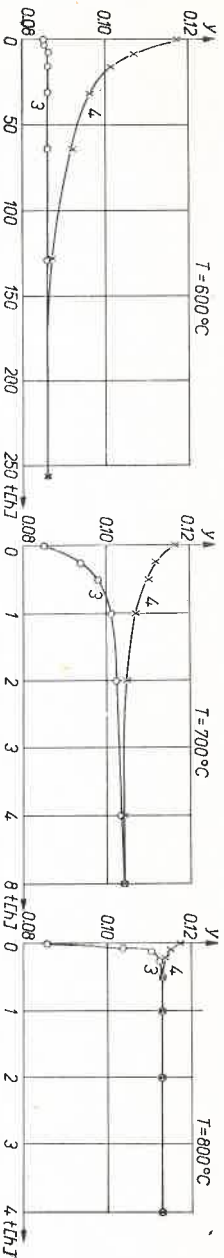

Fig. 6. Changes in the parameter y with annealing time for samples with $x = 1.25$; curve $3 - y(t)$ dependence for a slowly cooled sample annealed at 600, 700, and 800°C; curve $4 - y(t)$ dependence for a sample quenched from 1200°C and then annealed at 600, 700, and 800°C

2. The magnetic method of the investigation of diffusion processes presented in this paper can be applied to many magnetic materials, in particular to ferrimagnetics with several sublattices in which the migrating cations have different magnetic moments.

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