

MÖSSBAUER-EFFECT STUDY OF CALCIOMAGNETITES

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(Received September 23, 1997; in final form January 28, 1998)

$\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ samples, with $x \leq 0.28$, prepared from $\alpha\text{-Fe}_2\text{O}_3$ and CaO by the Bridgman method were investigated by means of ^{57}Fe Mössbauer spectroscopy. Room temperature spectra gave evidence that the samples were multiphase, the calciomagnetite being the dominant phase with a contribution of 73% to 99%, depending on the sample. Analysis of the subspectra associated with the calciomagnetite gave evidence that Ca-ions reside on the tetrahedral (A) sites and have not random distribution. Their presence on those sites causes a reduction of the hyperfine field at Fe nuclei occupying the octahedral positions (B) by 12.3(1.0) kOe per one Ca-ion and a decrease in the average hf field, $\langle H_B \rangle / dx$, at the rate of 29 kOe/mol% for $x \leq 0.07$ and of 387 kOe/mol% for larger x . In addition, a linear correlation between $\langle H_B \rangle$ and the average isomer shift, $\langle I_B \rangle$, was revealed to hold. It indicates that addition of Ca-ions into the magnetite causes a decrease in the spin-density and an increase in the charge-density at Fe nuclei occupying the B-sites.

PACS numbers: 76.80.+y, 82.80.Ej

1. Introduction

Magnetite, Fe_3O_4 , a member of the oxide spinels family, has been a subject of numerous investigations. Their comprehensive review is given elsewhere [1]. It contains one Fe^{3+} ion per formula unit on the tetrahedral site (A) and one Fe^{3+} and one Fe^{2+} ion on the octahedral site (B). There are two sound reasons for the interest in the compound: (i) scientific and (ii) technological. The former stems from the fact that magnetite represents a classical case of the ferrimagnetic structure, on which various theoretical models depicting phase transitions as well as exchange interactions can be tested and compared. The latter is due to the fact that magnetite, as a basic iron ore sinter, is important in the steel making industry.

Despite a vast body of experimental data and theoretical calculations that have been accumulated, there are still open problems related to the issue. Among them the question of the exchange integrals remains unsolved. There is here a general agreement that the interaction between Fe-ions goes via oxygen p orbitals, the so-called super exchange interaction, and that the A-B interaction dominates, but there is a rather large uncertainty concerning the values of the exchange integrals, J , as obtained from various experiments or calculations. There is also a strong disagreement as far as the A-A and B-B interactions are concerned: all possibilities i.e. positive, negative and zero values of J , with amplitudes one order of magnitude lower than that of the A-B interaction or even equal to it can be found [1-3]. It is also not clear whether or not the exchange integral for $\text{Fe}_A^{2+}-\text{Fe}_B^{3+}$ is different than the one for $\text{Fe}_A^{3+}-\text{Fe}_B^{3+}$. A possible reason for such situation may follow from the fact that physical properties of magnetite are very sensitive to the oxygen stoichiometry [4], which, in turn is a derivative of sample preparation and its history. To illustrate this let us take the results obtained by means of the Mössbauer spectroscopy which is a very useful tool to study the issue. The room temperature values of the hyperfine field scatter within the interval of 480-498 kOe for the A-site, and between 450-463 kOe for the B-site [5-14].

Substitution of Fe-ions by other cations results in a change of the physical properties of magnetite, hence it may provide a valuable information on the issue. In addition, by doping Fe_3O_4 one can study the nature of the ion substitution which is usually selective [1]. Doping by Ca-ions, a subject of the present investigation, is also important from the technological viewpoint as Ca-ions present in the iron ore sinters improve their sintering properties by increasing the reductibility.

The so-called calciomagnetites, $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$, were already studied by means of the Mössbauer spectroscopy [12-14]. However, the results obtained are not quite consistent, which may be partly due to different models of spectra analysis and partly to a different way of sample preparation. Consequently, it is reasonable and justified to carry out further investigation on them. By a careful analysis of the room temperature spectra with the use of various models we hope to shed more light and supply a new information on the issue.

2. Experimental

2.1. Sample preparation

Samples to be studied were prepared from hematite, $\alpha\text{-Fe}_2\text{O}_3$, and from calcium oxide, CaO, which is different than described elsewhere [12, 14]. Adequate quantities of both constituents to obtain calciomagnetite, $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$, were homogenized by mixing them in an agate mortar. The mixture was next pressed under a load of 50 kG/cm² into bars which were subsequently sintered at 1000°C for 4 to 5 h in air. The samples obtained in that way were finally remelted by the Bridgman method.

2.2. X-ray and microprobe analysis of the samples

The samples were analyzed by X-ray diffraction in order to determine the lattice constant of the calciomagnetite, a , and by microprobe analysis in order to

TABLE I

Lattice constant, a , and the effective concentration of Ca, x^* , of the investigated calciomagnetites, $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ as determined from X-ray diffraction.

x	0.04	0.08	0.12	0.16	0.20	0.28
a [Å]	8.410	8.425	8.430	8.431	8.435	8.443
x^*	0.03	0.07	0.10	0.11	0.12	0.15

determine the real concentration of Ca, x^* , in the structure of the calciomagnetite. The results obtained are displayed in Table I.

As can be seen from Table I the values of x^* are significantly lower than the corresponding nominal values, x , especially for the most concentrated samples. This means that in these samples there are other than calciomagnetite phases that contain Ca. The data shown in Table I give also evidence that the lattice constant of the calciomagnetite, a , is a linear function of x^* which indicates that Ca-ions occupy substitutional sites in the structure of the calciomagnetites.

2.3. Measurement of Mössbauer spectra

For Mössbauer-effect measurements the samples were ground into powder in the agate mortar and the spectra were collected at 295 K on samples containing $\approx 10 \text{ mgFe/cm}^2$. They are presented in Figs. 1, 2 and 3. Altogether 15 spectra were recorded, including three on samples that were used as standards for the identification of additional phases, and five on magnetite prepared in a different way. The remaining eight spectra were measured on the $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ phase with $x \leq 0.28$, nominally. The list of the investigated samples with their description is displayed in Table II.

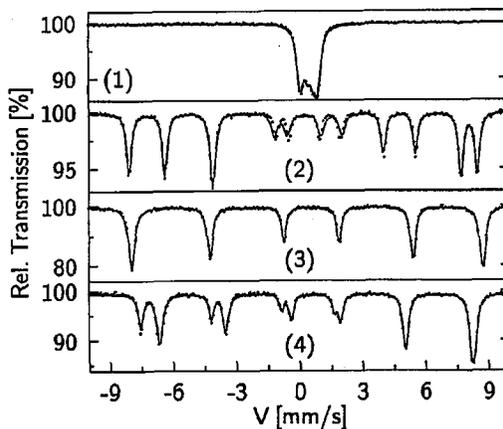


Fig. 1. ^{57}Fe Mössbauer spectra of the samples used as standards (samples no. 1-4) taken at 295 K. For their identification see Table II.

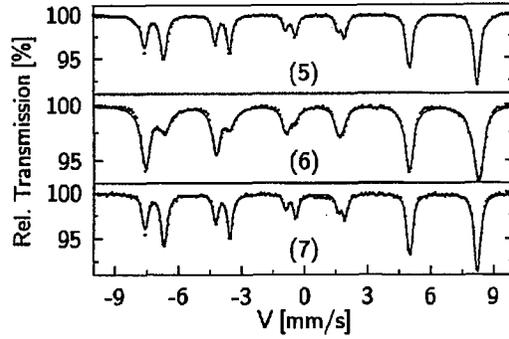


Fig. 2. ^{57}Fe Mössbauer spectra of magnetite with various history (samples no. 5–7) recorded at 295 K. For more details see Table II.

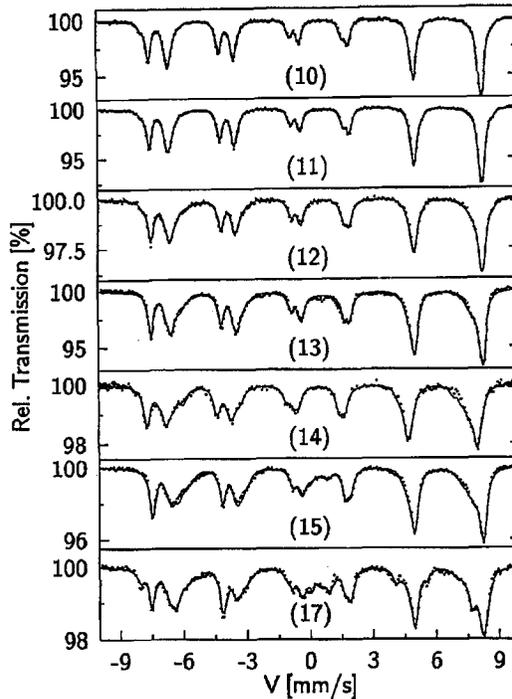


Fig. 3. ^{57}Fe Mössbauer spectra of calcimagnetites (samples no. 10–17) recorded at 295 K. For more details see Table II.

2.4. Analysis of the spectra

It follows from previous Mössbauer studies [12–14] that substitution of Ca-ions into magnetite structure results in the broadening of the lines of the B-sub-spectrum while the lines of the A-sub-spectrum remain unchanged. The previous authors accounted for this effect in three different ways. Hryniewicz et al. [12] chose the simplest way by fitting the overall spectrum with only two sex-

TABLE II

List of the investigated samples.

Sample no.	Sample	Remarks
1	CaOFe_2O_3	standard
2	$2\text{CaOFe}_2\text{O}_3$	standard
3	Fe_2O_3	standard
4	Fe_3O_4	standard
5	Fe_3O_4	once melted
6	Fe_3O_4	sintered
7	Fe_3O_4	once melted, "wings"*
8	Fe_3O_4	twice melted
9	Fe_3O_4	triple melted
10	$\text{Ca}_{0.04}\text{Fe}_{2.96}\text{O}_4$	once melted
11	$\text{Ca}_{0.08}\text{Fe}_{2.92}\text{O}_4$	once melted
12	$\text{Ca}_{0.12}\text{Fe}_{2.88}\text{O}_4$	once melted
13	$\text{Ca}_{0.16}\text{Fe}_{2.84}\text{O}_4$	once melted
14	$\text{Ca}_{0.20}\text{Fe}_{2.80}\text{O}_4$	once melted
15	$\text{Ca}_{0.28}\text{Fe}_{2.72}\text{O}_4$	once melted
16	$\text{Ca}_{0.16}\text{Fe}_{2.84}\text{O}_4$	twice melted
17	$\text{Ca}_{0.20}\text{Fe}_{2.80}\text{O}_4$	twice melted

*During the melting process a kind of "wings" were formed outside the sample core. These "wings" were measured as a separate sample.

tets. De Sitter et al. [13] fitted the B-sub-spectrum assuming only Ca-ions in the nearest-neighbour (nn) position are responsible for its broadening. In addition, the authors assumed that the distribution of Ca-ions was random. Finally, Gérardin et al. fitted their B-sub-spectra by means of the hyperfine distribution method [14]. It must be realized that all these three approaches have certain drawbacks, hence the results they yielded are biased or not precise enough. In particular, by fitting the B-sub-spectrum, which is very asymmetric, with only one sextet, the authors of Ref. [12] were not able to draw any conclusion on the influence of an individual Ca-ion on the spectral parameters, and, in addition, the information on the average values of the spectral parameters they extracted was not precise enough. The authors of Ref. [13] could not get information on the actual distribution of Ca-ions in the structure of magnetite, because they assumed the distribution was random. Finally, the authors of Ref. [14] did better than those of Ref. [12] as far as the average quantities are concerned, but they could not get any information on the effect of individual Ca-ions. Having all these drawbacks in mind we analyzed the spectra by means of the least-squares procedure using three different models: I, II and III.

- Model I: it was here assumed that the broadening of the subspectrum B is due to Ca-ions in the nn shell and the effect of one Ca-ion on the hyperfine field, H , and the isomer shift, I , is additive, i.e. $H_B(m; x) = H_B(0; x) + m\Delta H$ and $I_B(m, x) = I_B(0, x) + m\Delta I$, where $H_B(m; x)$ is the hyperfine field at Fe nuclei in the B-site having m Ca-ions in the nn shell, and ΔH is the shift of the hf field due to one Ca-ion. The meaning of the I -symbols is similar. The probability of a given configuration, $P(m, x)$, was calculated from the binomial distribution and set constant as in Ref. [13].
- Model II: it was basically similar to model I, except the $P(m, x)$ -values were treated as free parameters. This procedure made it possible to determine the actual probability of having various number of Ca-ions on the A-sites, hence to verify whether the real distribution of the dopant ions is random or not.
- Model III: within this model the subspectrum B was analyzed in terms of the hf field distribution method, i.e. similarly as in Ref. [14]. Although this way of analysis cannot supply so detailed information as I and II, it can be instead used to check the results yielded by I and II.

It has turned out that the best fits in terms of χ^2 values were yielded by model II with non-statistical distribution of Ca-ions as well as by model III. This

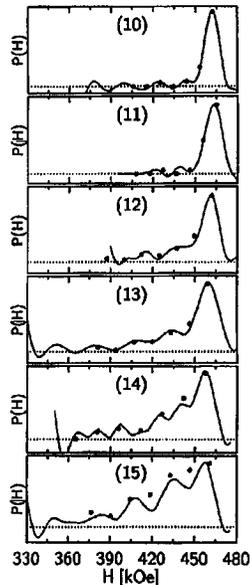


Fig. 4. Histograms of the hyperfine field distribution, $P(H)$, obtained from the spectra shown in Fig. 3 by means of model III (solid lines) with superimposed values of $P(H)$ (full circles) yielded by model II.

can be also well seen in Fig. 4 showing a comparison between the distributions of the hf fields obtained from model III and the discrete values of $P(H)$ yielded by model II. Consequently, in the following the results obtained with these two ways of spectra analysis will be presented and discussed.

2.5. The phase analysis

The spectra shown in Figs. 2 and 3 give a clear evidence that the samples are not single-phase. Their analysis enabled an identification of particular phases as well as a determination of their relative abundance. The latter was assumed to be proportional to a spectral area of a subspectrum ascribed to the given phase. It was here further assumed that the f -factor was identical for each phase present. This assumption may not be quite true as the values of f -factor depend on several circumstances such as the crystal structure of the phase, the degree of stoichiometry, and even the kind of the site within the given phase (e.g. for magnetite $f_A/f_B = 1.06 \pm 01$ at RT [15]). However, it is believed that eventual corrections would not be greater than errors of determination of the spectral parameters. For example, in the case of hematite, as the additional phase, its f -factor, $f_h = 0.837$ and that of magnetite, $f_m = 0.889$, both at RT [16]. This means that the actual abundance of hematite is larger than it follows from the spectral area only. If one takes into account the above-given values of f_A and f_B , then for the sample no. 5 one gets 92.3%, instead of 92.7% for magnetite and 7.7% instead of 7.3% for hematite. Such a difference is smaller than the error within which these quantities were determined.

Abundances of the identified phases in the investigated samples are listed in Table III. From the results presented there it follows that calciomagnetite is the dominant phase in the samples and its abundance ranges between 73% and 99%. Low concentrated samples, $x \leq 0.12$, contain in addition $\approx 5\%$ hematite. In more concentrated samples ($x \geq 0.16$), $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ phase is accompanied by the second phase in the form of CaOFe_2O_3 with the abundance between $\approx 0.7\%$ and $\approx 8\%$, except the sample no. 15, where $\text{Ca}_4\text{Fe}_9\text{O}_{17}$ exists as the second phase and its abundance reaches $\approx 19\%$. The sample no. 17 is the only one where two additional phases exist: (1) $\approx 8.5\%$ of CaOFe_2O_3 and (2) $\approx 18\%$ of $2\text{CaOFe}_2\text{O}_3$. The latter two samples were obtained by remelting the samples no. 13 and 14, respectively. The difference in the phase composition revealed for the samples no. 13, 14, 16, and 17 gives an evidence that the actual phase composition of the investigated samples depends on the sample history. It also follows from Table III that the highest abundance of the calciomagnetite was achieved by a single-melting process. Additional melting has led to a strong reduction of the abundance of $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ at the cost of other phases. This can be also well seen for undoped magnetite, where additional melting has resulted in an increase in hematite (samples no. 8 and 9). The results of the phase analysis also indicate that the actual concentration of Ca in the $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ phase is lower than the nominal value because of the formation of other Ca-containing phases. With the Mössbauer effect, only those containing Fe could have been detected, so it was not possible to determine in this way the content of Ca in the calciomagnetites.

TABLE III

Results of the phase analysis of the investigated samples as obtained based on model II and III. The figures denote the percentage of a given phase.

Sample no.	$\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$	Fe_2O_3	CaOFe_2O_3	$2\text{CaOFe}_2\text{O}_3$	$\text{Ca}_4\text{Fe}_9\text{O}_{17}$
1	–	–	100	–	–
2	–	–	–	100	–
3	–	100	–	–	–
4	100	–	–	–	–
5	93.9	6.1	–	–	–
6	100	–	–	–	–
7	100	–	–	–	–
8	90.4	9.6	–	–	–
9	84.7	15.3	–	–	–
10	94.6(II)	5.4(II)	–	–	–
	94.3(III)	5.7(III)	–	–	–
11	94.6(II)	5.4(II)	–	–	–
	95.2(III)	4.8(III)	–	–	–
12	98.0(II)	2.0(II)	–	–	–
	96.6(III)	3.4(III)	–	–	–
13	97.1(II)	–	2.9(II)	–	–
	96.8(III)	–	3.2(III)	–	–
14	99.5(II)	–	0.5(II)	–	–
	98.8(III)	–	1.2(III)	–	–
15	95.5(II)	–	4.5(II)	–	–
	95.4(III)	–	4.6(III)	–	–
16	80.5(II)	–	–	–	19.5(II)
	80.9(III)	–	–	–	19.1(III)
17	73.6(II)	–	8.1(II)	18.3(II)	–
	73.4(III)	–	8.8(III)	17.8(III)	–

3. Results and their discussion

3.1. Spectral parameters

The best-fit spectral parameters obtained with model II and III are displayed in Table IV. It can be seen that the presence of Ca-ions in the magnetite structure manifests itself by the decrease in the hyperfine field at Fe nuclei occupying the B-sites. One Ca-ion present on the A-site reduces this field on average by 12.3(1.0) kOe. This is much less than 30 kOe as reported in [13]. Such a behaviour of Ca-ions causes the average B-site hf field to decrease with x^* as shown in Fig. 5.

TABLE IV

Best fit spectral parameters of the investigated calciomagnetites as determined by the use of models II and III. Hyperfine fields, H , are in kOe, and isomer shifts, I , in mm/s. The uncertainties of H_B and ΔH are ± 0.5 kOe, of H_A is ± 1.3 kOe, of I_A , I_B and ΔI is ± 0.002 mm/s and that of n_B/n_A is ± 0.1 .

Model II									
x^*	$H_B(0; x)$	ΔH	$I_B(0; x)$	ΔI	n_B/n_A	$\langle H_B \rangle$	$\langle I_B \rangle$	H_A	I_A
0.00	462.1	—	0.816	—	1.46	462.1	0.816	493.9	0.418
0.03	462.5	-9.5	0.813	0.000	1.38	458.4	0.813	493.8	0.419
0.07	464.9	-9.5	0.808	0.020	1.42	460.0	0.819	494.0	0.416
0.10	461.8	-12.4	0.791	-0.004	1.46	448.7	0.787	492.2	0.419
0.11	458.8	-13.8	0.798	-0.010	1.41	442.7	0.787	492.2	0.416
0.12	457.7	-15.4	0.776	-0.006	1.65	438.4	0.769	489.9	0.424
0.15	458.6	-14.5	0.766	0.009	1.54	432.6	0.782	491.0	0.423
Model III									
0.00							—	—	
0.03							461.0	0.814	
0.07							460.9	0.817	
0.10							451.1	0.776	
0.11							437.5	0.793	
0.12							443.4	0.758	
0.15							433.4	0.792	

It can be seen that the decrease $d\langle H_B \rangle/dx^*$ is not constant, but rather two ranges exist: first, for $x^* \leq 0.07$ the decrease is slow and it is equal to 29 kOe/mol%, and second, for $x^* \geq 0.07$, $\langle H_B \rangle$ decreases rapidly with the slope of 387 kOe/mol%. The initial rate of decrease agrees pretty well with that reported in Ref. [12]. It must be, however, realized that the authors of that paper analyzed their spectra with two sextets only and they calculated the decrease in $\langle H_B \rangle$ in terms of the nominal concentration of Ca which, as shown in the present study, drastically may differ from the real content of Ca in the structure of magnetite. These two factors are obviously responsible for the big difference in the rate of decrease in $\langle H_B \rangle$. Also the average isomer shift associated with Fe nuclei on the B-sites, $\langle I_B \rangle$, exhibits similar dependence on x^* , indicating thereby that their charge-density is affected by the substitution. There is a nice linear correlation between $\langle H_B \rangle$ and $\langle I_B \rangle$, as illustrated in Fig. 6. Its slope is equal to 584 kOe s/mm and the correlation coefficient $r = 0.95$. The decrease in $\langle H_B \rangle$ and $\langle I_B \rangle$ with x^* means that there is an effective charge transfer from Fe nuclei on B-sites caused by the Ca-substitution. Taking into account that the difference of 0.4 mm/s between I_A and I_B is associated with the difference of 0.5 electrons, one can estimate the maximum charge transfer for ≈ 0.07 electrons in the case of the most concentrated calciomagnetite.

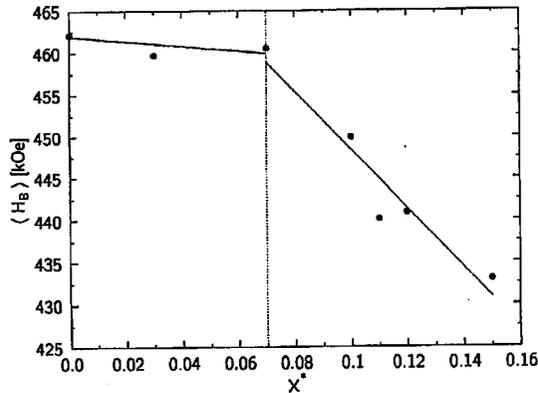


Fig. 5. The average hf field at Fe nuclei on B-sites $\langle H_B \rangle$ (averaged over the values obtained from models II and III) versus the effective content of Ca in the magnetite structure, x^* . The straight lines represent the best fits to the data in the two ranges.

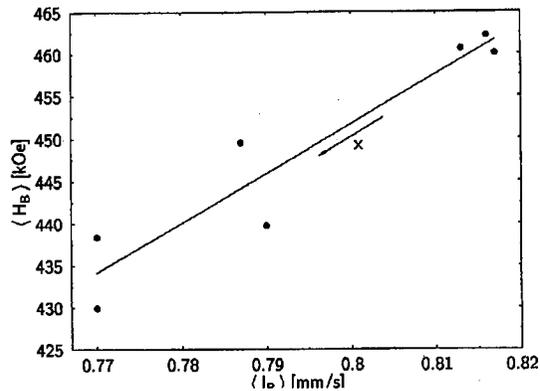


Fig. 6. The average hf field, $\langle H_B \rangle$, as a function of the average isomer shift, $\langle I_B \rangle$. The straight line is the best fit to the data and has a slope of 587 kOe s/mm. The arrow shows the direction in which x increases.

It is also clear from Table IV that the spectral parameters of Fe nuclei sitting on the A-sites are independent of Ca content. This can be taken as evidence that the exchange integral J_{A-A} is vanishingly small. This supports some theoretical calculations [2, 3] but is at variance with other results [1, 17, 18]. The constancy of I_A also means that the changes of $\langle I_B \rangle$ with x^* are related with the charge transfer not with the expansion of the lattice due to the substitution.

3.2. Localization of Ca-ions in magnetite

There are two non-equivalent lattice sites in the crystallographic structure of magnetite: the tetrahedral site, called A, and the octahedral site, called B. There are 32 A-sites in an unit cell, from which 8 are occupied by metallic cations, and

TABLE V

Coordination number, the type of the nearest neighbours, and the relative population for the sites A and B in the structure of magnetite.

Site	CN(nn)	Relative population
B	6B+6A	2
A	12B	1

64 B-sites, from which 16 are occupied by metallic cations. From the viewpoint of the Mössbauer effect, the pertinent quantity is the coordination number of the cations, CN. If one confines itself to the nearest-neighbours, which is justified in the light of theoretical calculations and experimental data on the exchange integrals [1-3], then the situation is as the one displayed in Table V. It follows from it that CN is the same for the both sites. However, all nn-atoms of the A-site have the octahedral symmetry, while the B-sites "see" in the nn shell 6 octahedral and 6 tetrahedral atoms. Thanks to this difference, which causes that the spectral parameters for both sublattices are different, it is possible to draw information from the Mössbauer spectra on the selective substitution of Fe atoms by dopants. The presence of a Ca-ion in the given sublattice should manifest itself by a change of the spectral parameters in a subspectrum which parameters are sensitive to this presence. In particular, one should observe a change of the hyperfine field, H , the isomer shift, I , and the relative intensity of the given subspectrum. The values of the exchange integrals, J_{A-A} , J_{B-B} , and J_{A-B} decide which subspectrum reflects the presence of Ca-ions in the structure and on which site. This offers an unique opportunity to draw conclusions on the exchange integrals and on the selective substitution from the spectral parameters.

The influence of the Ca-dopant manifests itself at most in the outermost lines of the spectrum. Inspection of these lines shown in Fig. 7 gives a clear evidence that Ca-ions present in the structure of magnetite disturb predominantly the B-subspectrum. This may occur if, at least, one of the two integrals, viz. J_{A-B} and $J_{B-B} \neq 0$. At the same time one observes that the A-subspectrum remains unchanged upon Ca-substitution. Indeed, its line width at half maximum, Γ_A , does not depend on the concentration of Ca and is equal to 0.31(1) mm/s which agrees well with the corresponding value in Ref. [13]. Such a behaviour means that either (1) Ca-ions are present on the B-site only, and $J_{A-B} = 0$, and the broadening of the line is due to $J_{B-B} \neq 0$, or (2) they are present on the A-site only and $J_{A-A} = 0$, and $J_{A-B} \neq 0$. The first conclusion is at variance with the theoretical calculations and experimental results that $J_{A-B} \gg 0$ [1-3]. Consequently, it seems justified to conclude that Ca-ions substitute for the A-site exclusively, which agrees with previous conclusions [12-14], too. However, in addition to the previous works on the issue, the present analysis (i) gives a clear evidence that the distribution of Ca-ions among the A-sites is not random — see Sec. 3.3, and (ii) it supplies the value of the shift of the B-site hf field due to one Ca-ion on the A-site $\Delta H = -12.3(1.0)$ kOe, which disagrees with that given in Ref. [13].

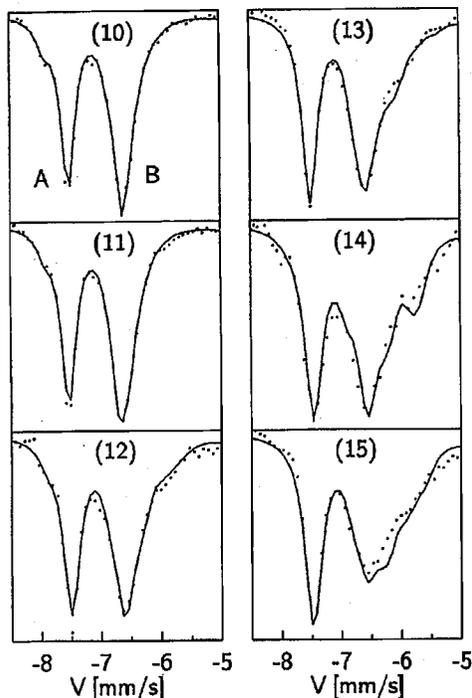


Fig. 7. The outermost lines of the subspectra shown in Fig. 3. Note the broadening of the subspectrum B.

Another effect that accompanies the substitution of Fe-ions in the structure of magnetite is a change of the intensity of the subspectra corresponding to the two sublattices. For a pure stoichiometric magnetite the ratio between the Fe-ions on the B-sublattice, n_B , and those on the A-sublattice, n_A , is equal to 2. In the magnetite where a fraction x of Fe atoms has been substituted by a foreign X atoms this ratio is equal to

$$\left(\frac{n_B}{n_A}\right)_A = \frac{2}{1-x} \quad (1)$$

if X-ions occupy the A-sites, exclusively. If, however, X-ions have substituted Fe-ions on the B-site only, then this ratio would be given by

$$\left(\frac{n_B}{n_A}\right)_B = 2 - x. \quad (2)$$

Finally, if X-ions were localized on both sites with frequency proportional to their population the ratio would stay constant and be equal to 2, independently of x .

The fitting of the spectrum of magnetite prepared by a single-melting process (sample no. 5) yielded $n_B/n_A = 1.46$ instead of 2. Similar values of the ratio were revealed for the calciomagnetites — see Table IV. The big difference may be explained in terms of the great departure from the stoichiometry on the B site

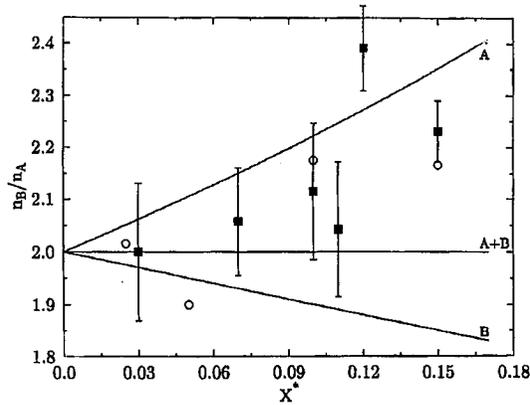


Fig. 8. The ratio of Fe-ions on B-site to that on A-site, n_B/n_A , versus Ca-content, x^* , expected from Eq. (1) — curve A, and Eq. (2) — line B, as well as its values determined experimentally in the present work (squares) and in Ref. [13] (circles). The uncertainties of the n_B/n_A -values are shown as error bars.

and/or an oxidation of the calciomagnetites during the sample preparation. The net effect of the latter process is a reduction in the intensity of the B-sub spectrum, hence the n_B/n_A ratio [19, 20]. However, it is not possible to separate the two reasons from the present experiment. Consequently, it is not easy to justify on the selective substitution of Ca-ions based on the present results in terms of Eqs. (1) and (2). Assuming, however, the degree of the stoichiometry for the all calciomagnetites studied is the same, one can correct for it by multiplying the measured values of the n_B/n_A ratios by 1.45 ($= 2/1.38$). The values of the experimentally determined ratios of n_B/n_A normalized in this way are displayed in Fig. 8 together with their behaviour expected from Eqs. (1) and (2). It can be seen that they show an increasing trend with x^* , i.e. along the A-line, which gives a further argument in favour of the localization of Ca-ions on the A-sites. It must be here, however, remembered that the above-made normalization was rather arbitrary. For comparison, the results obtained by Gérardin and co-authors [14] are also displayed in that figure.

3.3. Distribution of Ca-ions over the A-sites

Analysis of the spectra recorded for the calciomagnetites by the use of model II enabled a determination of the distribution of Ca-ions among the A-sites of the structure. The results obtained are illustrated in Fig. 9 which shows a comparison between the measured probabilities of having none, $P(0)$, one, $P(1)$ and two, $P(2)$ Ca-ions on the A-site (full circles), and their corresponding values expected for a random distribution (full lines). It is clear that the actual distribution is not random, especially for the more concentrated ($x > 0.07$) samples. One observes, namely, that for these samples the measured $P(1)$ -values are significantly smaller, and those of $P(2)$ are significantly greater than expected from the binomial distribution. This indicates that the substituting of one Ca-ion is associated with some "repulsion". The values of $P(0)$, however, follow the random distribution.

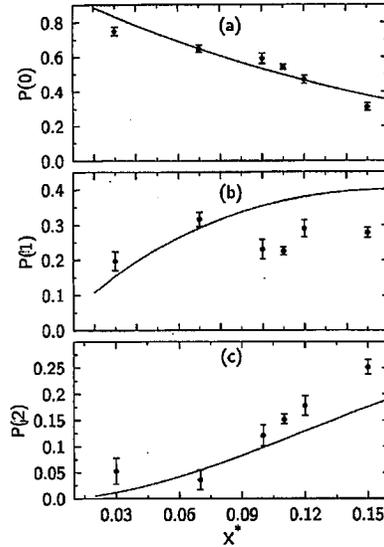


Fig. 9. Distributions of Ca-ions on A-sites of the magnetite structure. The probability of having none Ca-ion, $P(0)$, is shown in (a), that of one Ca-ion, $P(1)$ in (b), and that of two Ca-ions, $P(2)$ in (c). Solid circles stand for the P -values obtained in the present work by fitting the spectra with model II, and the solid lines represent the behaviour expected for the random distribution. The uncertainties of the P -values are indicated by error bars.

4. Summary and conclusions

A series of samples prepared by the Bridgman method from sintered α - Fe_2O_3 and CaO was investigated by means of the Mössbauer spectroscopy which revealed a multi-phase composition of the final samples with 73% to 99% contribution of calcimagnetite. The analysis of the subspectra associated with $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ made it possible to draw the following conclusions:

- Ca-ions substitute for Fe-ions on the tetrahedral (A) sites only and their simultaneous presence on the octahedral (B) sites must be excluded in the light of the value of the exchange integral, J_{A-B} .
- The distribution of Ca-ions is not random and the actual number of these ions on A-sites is significantly smaller than expected from the binomial distribution, especially for $x^* > 0.07$.
- The presence of Ca-ions on A-sites causes a reduction of the B-site hf field by 12.3(1.0) kOe per one Ca-ion and the decrease in the average hf field with the rate of 29 kOe/mol% for $x^* \leq 0.07$ and 387 kOe/mol% for larger x^* .
- The isomer shift associated with Fe nuclei on B-sites shows a similar behaviour versus x^* which manifests itself in a linear correlation with the corresponding hf field having a slope of 584 kOe s/mm.

- Doping magnetite with Ca results in the decrease in the spin- and charge-density at Fe nuclei on octahedral sites.

The second and the third item is new compared to earlier publications, while the other three items confirm previous results.

Acknowledgment

The investigation was in part supported by the Committee for Scientific Research within the project No. PB 1644/3/91.

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