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Mössbauer-Effect Study of Ca-Substituted Magnetites

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Abstract. $Ca_xFe_{3-x}O_4$ samples, with $x \leq 0.28$, prepared from $\alpha-Fe_2O_3$ and CaO by the Bridgeman method were investigated by means of ^{57}Fe Mössbauer spectroscopy. Room temperature spectra gave evidence that the samples were multi-phase with 73% to 99% contribution of the calcimagnetite, depending on the sample. Analysis of the subspectra associated with the calcimagnetite enabled to conclude that Ca-ions reside on the tetrahedral (A) sites and have not random distribution. They reduce the hyperfine field at Fe nuclei occupying the octahedral positions (B) by 12.3(1.0) kOe per one Ca-ion and cause a decrease of the average hyperfine 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 . A linear correlation between $\langle H_B \rangle$ and the average isomer shift $\langle I_B \rangle$ was revealed to hold. It permitted to conclude that Ca-doping causes a decrease of the spin-density and an increase of the charge-density at Fe nuclei occupying the B-sites of magnetite.

Magnetite, Fe_3O_4 , a member of the oxide spinels family, has been a subject of numerous investigations [1]. There are two main 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, 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 which, at least partly, stem from a large spread of data, which sometimes are at variance with each other.

A possible reason for such situation may follow from the fact that physical properties of magnetite are very sensitive to the oxygen stoichiometry [2], 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 only, which is a very useful tool to study ferrites. The room temperature values of the hyperfine (hf) field scatter within the interval of 480-498 kOe for the A-site, and between 450-463 kOe for the B-site [3,4,5,6].

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 subject. 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 view point as Ca-ions present in the iron ore sinters improve their sintering properties by increasing the reductibility.

Samples described here were prepared from hematite, $\alpha-Fe_2O_3$ and from calcium oxide, CaO . Adequate quantities of both constituents to obtain calcimagnetite were homogenized by mixing 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 were finally remelted by the Bridgeman method.

The lattice constant of the calcimagnetites, a was determined by the x-ray diffraction and the real content of Ca in the structure, x^* by the microprobe analysis. The latter was significantly lower than the nominal value, x .

The Mössbauer spectra collected at 295K (for a typical ones see Fig. 1) gave a clear evidence that the samples were multi-phase. The analysis of the spectra made it possible to identify particular phases as well as to determine their relative population. For the latter it was assumed that the f -factor was the same for each phase present. Calcimagnetite turned out to be the dominant phase with a share of 73% to 99%.

The presence of Ca-ions in the magnetite structure manifests itself in the decrease of the hf 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 [4]. Such a behaviour of Ca-ions causes the average B-site hf field, $\langle H_B \rangle$ to decrease with x^* .

Also the average isomer shift of Fe nuclei on the B-sites, $\langle I_B \rangle$ exhibits similar dependence on x^* , as $\langle H_B \rangle$ does, 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 shown in Fig. 2. Its slope is equal to 584 kOe/mm/s and the correlation coefficient $r=0.95$. The decrease of $\langle H_B \rangle$ 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. 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 [7] but is at variance with other results [8,9].

Fig. 1: ^{57}Fe Mössbauer spectra of $\text{Ca}_x\text{Fe}_{3-x}\text{O}_4$ recorded at 295K for (a) $x^* = 0.07$ and (b) $x^* = 0.12$.

Fig. 2: The average hf field, $\langle H_B \rangle$ as the 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/mm/s. The arrow shows the direction in which x increases.

Analysis of the spectra also permitted to conclude that Ca-ions substitute for the A-site exclusively, which agrees with previous conclusions [4,5,6], too. However, in addition to the previous works, the present analysis (i) gives a clear evidence that the distribution of Ca-ions among the A-sites is not random, 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.

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