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A Mössbauer study of Al and Ga substituted magnetite

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A Mössbauer study of Fe$_{1-x}$Al$_x$O$_4$ and Fe$_{1-x}$Ga$_x$O$_4$ has been undertaken. Measurements at low temperatures in magnetic fields enabled us to better separate the Fe(A) and Fe(B) subspectra and to determine the cation distribution on the sublattices of the spinel structure, whereas Ga$^{3+}$ replaces only Fe$^{3+}$ on the A sites for $x<0.3$ and then starts to distribute itself over both A and B sites.

In order to better characterize the cation distribution in the spinel lattice of Al and Ga substituted magnetite and its influence on the hyperfine fields HF(A) and HF(B) at the Fe(A) and Fe(B) sites, a Mössbauer study in which the emphasis was put on measurements in relatively high magnetic fields at low temperature, has been undertaken. In such a way it was possible to better separate the Fe(A) and Fe(B) Mössbauer subspectra and to determine the contribution of the different local environments of the Fe ions to the broadening of the Fe(B) subspectrum with increasing Al and Ga concentration.

EXPERIMENT

Polycrystalline samples of Fe$_{1-x}$Al$_x$O$_4$ (0.4 < $x$ < 1.4) have been prepared by sintering spray roasted mixtures of iron and aluminum sulfates at 1300 °C in an adjusted atmosphere to preserve the spinel structure; the partial oxygen pressures during the sinter process ranged from 100 atm (atm) = -4.9 for $x = 0$ till -7.5 for $x = 1.4$. The gallium ferrites Fe$_{1-x}$Ga$_x$O$_4$ (0.1 < $x$ < 1.2) have been prepared by standard ceramic techniques; the final sintering process was carried out at 1370 °C in CO$_2$/CO mixtures with a partial oxygen pressure of 10$^{-9}$ atm.

Mössbauer spectra were taken with conventional equipment, using cryostats for measurements at 77 and 4.2 K and a superconducting coil for applying fields up to 50 kOe in the direction of the gamma rays. A Mössbauer Fe/Rh source with an activity of 25 mCi was used.

RESULTS AND DISCUSSION

Fe$_{3-x}$Al$_x$O$_4$

The room temperature Mössbauer spectra for $x > 0.8$ show signs characteristic of relaxation spectra, $x = 1.4$ is already paramagnetic, in good agreement with the observations of Dehe $et$ al.$^1$ Spectra taken at 4.2 K do not show relaxation effects. The Fe(A) and Fe(B) subspectra overlap each other, and the relative intensities of the second and fifth peaks increase anomalously with Al concentration.

In order to improve the separation of the Fe(A) and Fe(B) subspectra, and to check the possibility of the existence of spin canting effects, Mössbauer spectra have been taken at 4.2 K in external fields of 10, 30, and 50 kOe applied parallel to the direction of the gamma rays. In the absence of any spin canting effects, the peaks corresponding to the Mössbauer lines 2 and 5 have to vanish.

In fact, that is actually the trend taken from Fig. 1. Because of the broadening of the Fe(B) lines, a good separation of the Fe(A) and Fe(B) subspectra is reached only in a field of 50 kOe.

A most peculiar aspect is the presence of a Mössbauer subspectrum with HF values varying from about 300 to 230 kOe with increasing $x$ in the range 0.6 < $x$ < 1.4. Its intensity is practically unaffected by the magnetic field, but increases strongly with $x$ in the range 0.8 < $x$ < 1.4. This subspectrum overlaps with lines 2 and 5 of the Mössbauer spectrum taken without a field, and obviously its presence explains the already mentioned anomalously strong intensity of these lines with increasing $x$. Therefore this spectrum is not evidence for spin canting but, as we believe, for Fe$^{3+}$ located at the A sites.

A further argument for this interpretation is that in an external field it shifts to larger velocities, as the Fe$^{3+}$(A) lines do, because the outer field adds to the HF of Fe(A) ions. This trend changes for $x = 1.4$, where both the Fe$^{3+}$(A) and Fe$^{2+}$(A) lines shift to lower velocities. The reason is that slightly below $x = 1.4$ the magnetizations of the Fe(A) and Fe(B) sublattices cancel each other and at $x = 1.4$ the external field will be parallel to the magnetization of the Fe(A) sublattice and therefore antiparallel to HF at the Fe(A) sites.

Whereas the Fe$^{3+}$(A) lines remain relatively narrow even for high $x$ values and HF at 4.2 K changes in the range 0.6 < $x$ < 1.2 from 520 to 480 kOe, the Fe(B) lines considerably broaden, especially in the range 0.6 < $x$ < 1.0.
An analysis of the dependence of the intensities of the Fe$^{3+}$ (A) and Fe$^{2+}$ (A) subspectra on $x$ shows that up to $x = 1.2$, because of a strong preference for octahedral sites, Al substitutes practically only Fe$^{3+}$ (B) ions in good agreement with other authors.\(^1\)

**Fe$_{3-x}$Ga$_x$O$_4$**

The room temperature Mössbauer spectra for $x \geq 1.0$ show the presence of strong relaxation effects. For $x < 0.7$ no relaxation occurs and in the negative velocity range the first Fe(A) line is relatively well separated from the Fe(B) one. This advantage is lost at 77 K but at this temperature no more relaxation effects for $x > 1.0$ occur. In order to better separate the Fe(A) and Fe(B) subspectra Mössbauer spectra
in an external field of 50 kOe have been taken at room temperature for \( x<0.7 \) and 77 K for \( x=1.0 \) and 1.2, as shown in Fig. 2.

In contrast to \( \text{Fe}_3 \text{Al}_4 \text{O}_4 \) there is no evidence for \( \text{Fe}^{2+} \) on \( \text{A} \) sites, i.e., the substitution with \( \text{Ga} \) at least up to \( x=1.2 \) does not displace \( \text{Fe}^{2+} \) from \( \text{B} \) to \( \text{A} \) sites and the cation distribution formula can be written as follows:

\[
\text{Fe}_{1-x+y} \text{Ga}^3_0 \left[ \text{Fe}^{2+}_x \text{Fe}^{3+}_y \right] \text{Ga}^3_0 \text{O}_4^-.
\]

From the intensities of the \( \text{Fe}(\text{A}) \) and \( \text{Fe}(\text{B}) \) subspectra a linear dependence of the form \( \alpha = 0.376 \, x \) has been derived, showing that \( \text{Ga}^{3+} \) distributes on both \( \text{A} \) and \( \text{B} \) sites even at very low concentration as \( x=0.1 \). Whereas the width of the \( \text{Fe}(\text{A}) \) Mössbauer lines does not change too much with \( x \), a strong asymmetrical broadening of the \( \text{Fe}(\text{B}) \) lines increasing with \( x \) takes place. The number of \( \text{Fe}(\text{B}) \) subspectra fitted changes from one for \( x=0.1 \) up to four for \( x\geq 0.4 \). The room temperature values of \( \text{HF}(\text{B}_i) \) for the subspectra indexed with \( \text{A} \) and \( \text{B}_i (i=0,1,2,3) \) for \( x<0.7 \) and the 77 K \( \text{HF}(\text{B}_i) \) values for \( x=1.0 \) and 1.2 are shown in Fig. 3. The trend is similar to that observed in the case of low \( \text{Cr} \) substitution in the \( \text{Fe}_{3-x} \text{Cr}_x \text{O}_4 \) system. The main reason for the occurrence of 4 \( \text{Fe}(\text{B}) \) subspectra is in our opinion the increasing ratio of the number of \( \text{Fe}^{2+}(\text{B}) \) to that of the \( \text{Fe}^{3+}(\text{B}) \) nearest neighbors with increasing \( x \) and \( \alpha \), because of the random distribution of \( \text{Ga}^{3+} \) ions on the \( \text{B} \) sites. Whereas the \( \text{A} \) and \( \text{B}_0 \) subspectra describe pure \( \text{Fe}^{3+} \) states, the subspectra \( \text{B}_1, \text{B}_2, \) and \( \text{B}_3 \) arise because of the increasing with \( x \) probability of finding environments with 2 \( \text{Fe}^{3+} \) and 3 \( \text{Fe}^{2+} \), 1 \( \text{Fe}^{3+} \), and 3 \( \text{Fe}^{2+} \) and only 3 \( \text{Fe}^{2+} \) iron nearest neighbors. The decrease of \( \text{HF}(\text{B}_i) \) in the sequence \( \text{B}_0 \to \text{B}_3 \) results from the increasing \( \text{Fe}^{2+} \) character of the hyperfine field. The general decreasing trend of all \( \text{HF}(\text{B}_i) \) values with \( x \) is due to the weakening of \( \text{A}-\text{B} \) exchange interaction because of the substitution of \( \text{Fe}^{3+}(\text{A}) \) magnetic active ions with the nonmagnetic \( \text{Ga}^{3+} \).

The intensities of the \( \text{Fe}(\text{B}_i) \) subspectra are in agreement with the expectations of a model in which one ascribes the \( \text{HF}(\text{B}_i) \) values to the types of environments mentioned before, assuming that their populations are given by the binomial distribution of the fraction \( \alpha \) of \( \text{Ga}^{3+} \) ions on the \( \text{B} \) sites.

According to this model, \( \text{HF}(\text{B}_i) \) has the quasipure \( \text{Fe}^{3+} \) character, whereas \( \text{HF}(\text{B}_0) \) has to derive from an admixture of equal amounts \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) states as in the case of the \( \text{Fe}(\text{B}) \) subspectrum of \( \text{Fe}_3 \text{O}_4 \).

\[\text{HF}(\text{B}_i) \]