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MÖSSBAUER EFFECT FOR Fe⁵⁷ PRODUCED BY THE DECAY OF Co⁵⁷ DOPED SELECTIVELY IN B SITES OF MAGNETITE

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Résumé. — Le spectre d'émission de Fe₃O₄ dopé par ⁵⁷Co a été relevé. On a trouvé qu'un ion Co substitue sélectivement un ion Fe dans les sites B de Fe₃O₄. Le spectre d'émission était analogue à celui du site B dans le spectre d'absorption au-dessus et en dessous de T_{∇} . La distribution de charge des ions Fe stabilisés après la décroissance de ⁵⁷Co est identique à celle des ions Fe dans la matrice de magnétite.

Abstract. — The Mössbauer emission spectrum was observed for Fe_3O_4 doped with Co⁵⁷. A Co ion was found to substitute selectively for an Fe ion in B site of Fe_3O_4 . The emission spectrum was similar to that of the B site in the absorption spectrum above and below T_V . The charge distribution of Fe ions stabilized after the decay of Co⁵⁷ is the same as that of Fe ions in B sites of the host magnetite.

1. Introduction. — Magnetite Fe_3O_4 is a ferrimagnetic inverse spinel. The tetrahedral (A) sites are occupied by Fe^{3+} ions and the octahedral (B) sites by Fe^{2+} and Fe^{3+} ions. Above the Verwey temperature $T_{\rm v}$ of $\simeq 119$ K, Fe²⁺ and Fe³⁺ ions in B sites have been known to exchange their electrons rapidly. Two kinds of Mössbauer spectra corresponding to the A site irons and to the B site irons, respectively, are observed in the temperature region $T_{\rm C} > T > T_{\rm y}$. At $T_{\rm y}$ a phase transition is occurred and the considerable changes in several physical properties are observed. The decreased electrical conductivity by a factor of ~ 100 below $T_{\rm v}$ is associated with the stop of the electron exchange. Verwey predicted the model that Fe^{2+} and Fe^{3+} ions in B sites are separately ordered and the crystal distorts to the orthorhombic symmetry [1]. However, many authors have shown that Verwey order is too simple to explain the Mössbauer spectrum at low temperatures [2-6]. Several models have been proposed but there are still ambiguities in the properties of Fe ions in B sites. Hargrove et al. interpreted the B site spectrum with 4 sites [4], and Rubinstein et al. with 5 sites [5]. We report the result of investigations with samples which show only a B site spectrum of magnetite. Lack of an A site spectrum makes the analysis much simpler.

We are also interested in the charge state of iron atoms produced by the decay of Co^{57} above and below $T_{\rm V}$.

2. Experimentals. — If a Co ion is diffused into Fe_3O_4 at high temperature, the Co^{2+} ion is expected to substitute selectively for an Fe ion in B sites from the fact that Co^{2+} ions in $CoFe_2O_4$ are known to be

located mainly in B sites [7, 8]. The powder and single crystal samples doped with Co^{57} were prepared using natural and synthetic Fe_3O_4 as host materials. We did not find any differences between the absorption spectra obtained for the natural Fe_3O_4 and the synthetic one.

(1) The carrier free Co^{57} was diffused into the powder, which was obtained by grinding natural crystals, at 1150 °C for 4 hours in an evacuated quartz tube.

(2) $\text{Co}^{57}\text{Cl}_2$ dropped on a (100) plane of a synthetic single crystal was diffused into the crystal at 950 °C for 30 min in an evacuated quartz tube:

In both cases, quartz tubes of a small volume (less than 1 cm³) were used to minimize oxidization of the samples by residual oxygen in the tubes. At room temperature the absorption spectrum obtained for the powder sample doped with Co^{57} showed essentially the same spectrum than that obtained for the undoped powder sample (Fig. 1*a*). This fact showed that the samples were not affected during the diffusing procedure of Co^{57} into them.

Both a constant acceleration Mössbauer spectrometer and a sinusoidally driven Mössbauer spectrometer were used. Co^{57} in Cu was used as a source to obtain the absorption spectra and Na₄Fe(CN)₆.10 H₂O was used as an absorber to obtain the emission spectra.

3. Results and discussions. — The spectra observed at room temperature for a powder sample doped with Co^{57} are shown in figure 1. Figure 1*a* is the absorption spectrum resulting from the use of the sample as an absorber, and figure 1*b* is the emission one resulting from the use of the sample as a source. Doppler velo-



FIG. 1. — Mössbauer spectra of powder Fe₃O₄ doped with Co³⁷ obtained at room temperature. A constant acceleration spectrometer was used. *a*) Absorption spectrum. Co⁵⁷ in Cu was used as a source. *b*) Emission spectrum périod Na₄Fe(CN)₆.10 H₂O was used as an absorber. The Doppler velocity including isomer

shift is normalized to the spectrum shown in a).

city including isomer shift for the latter is normalized to that for the former. The figure shows that the emission spectrum coincides with the absorption spectrum of the B site.

This result shows that Co^{57} diffused into Fe_3O_4 is located in B sites as expected. Another interesting conclusion is also derived : A multiply ionized Fe atom produced by the Auger process after the decay of Co^{57} is neutralized to Fe^{3+} or Fe^{2+} and takes part in the charge exchange between Fe^{2+} and Fe^{3+} in B sites of the host magnetite within the nuclear life of Fe^{57} excited state $(10^{-7} s)$.

The internal magnetic field at Fe nuclei in B sites is derived to be 464 kOe and agrees well with the value previously reported for the absorption experiment [2, 9].

The absorption spectrum for the powder sample obtained at 77 K is shown in figure 2a. This spectrum is quite similar to those previously reported [2, 4, 5].

The emission spectra obtained for a single crystal sample at room temperature and 77 K are shown in figure 3a and b, respectively. Gamma-rays are perpendicular to the (100) plane on which Co⁵⁷ ions are diffused. At room temperature the magnetic easy axis is known to be a < 111 > direction, so the expected intensity ratio of the spectrum is 3:2:1:1:2:3independently of the domain distribution. The spectrum at room temperature shown in figure 3a is similar to that of the powder sample (Fig. 1b), and its intensity ratio is approximately 3:2:1:1:2:3. The magnetic easy axis is changed to a < 100 > direction at the temperature ($T_{\rm R} \simeq 136 \, {\rm K} > T_{\rm V}$) where the anisotropy constant K_1 changes its sign from negative to positive with decreasing temperature. The efore, the intensity ratio of the spectrum at 77 K depends on the domain distribution of the surface of the crystal. In the spec-



FIG. 2. — a) Mössbauer absorption spectrum of powder Fe_3O_4 obtained at 77 K. A constant acceleration spectrometer was used. b) Mössbauer absorption spectrum for B sites. It was obtained by subtracting the A site spectrum from the spectrum shown in a).



FIG. 3. — Mössbauer emission spectra of single crystal sample doped with Co⁵⁷. Gamma-rays are perpendicular to the (100) plane on which Co⁵⁷ is diffused. A sinusoidally driven spectrometer was used.

trum shown in figure 3b, the intensity of the second and the fifth lines is considerably enhanced in comparison to that found for the powder sample. For another single crystal (¹) we observed a considerably reduced intensity for the second and the fifth lines. The preferred orientation of domains at the surface of the samples perhaps depends on the individual crystal used and on the condition of cooling. The spectrum obtained for each sample was reproducible. The source intensity of our powder sample is too weak to obtain the spectrum with good statistics at 77 K. Thus, we will only discuss the spectrum obtained for the single crystal in due consideration of the enhanced intensity of the second and the fifth lines.

(1) Co⁵⁷ was diffused at 1 050 °C for 30 min on a (100) plane of the crystal.

The emission spectrum observed at 77 K was compared with the B site spectrum which was obtained by subtracting the A site one from the experimental absorption spectrum at 77 K (Fig. 2b). The assignment of the line positions of the A site spectrum was done according to reference [4]. The agreement between figure 3b and figure 2b is fairly good. The characteristic lines for Fe^{2+} , which were assigned to belong to the different Fe^{2+} sites (I) and (II) in the absorption spectrum [4], are clearly seen in the emission spectrum and are indicated by $(I_6)_s$ and $(II_5)_s$ in figure 3b. This result shows that both Fe^{2+} and Fe^{3+} are stabilized in Fe_3O_4 below T_V after the decay of Co^{57} , in contrast with the result for $CoFe_2O_4$ labeled with Co^{57} where only Fe³⁺ is stabilized [8]. The intensity of the lines $(I_6)_s$ and $(II_5)_s$ is approximately similar to that of the lines $(I_6)_a$ and $(II_5)_a$ in the absorption spectrum. This fact indicates that the ratio of Fe²⁺ and Fe³⁺ produced by the decay of Co^{57} is approximately the same than

that of Fe^{2+} and Fe^{3+} in B sites of magnetite. The ordering scheme of Fe^{2+} and Fe^{3+} ions in B sites of magnetite has not been definitely determined. However, the ordering of Fe^{2+} and Fe^{3+} ions in B sites is considered by several authors [6, 10]. Therefore, one possible interpretation is that an Fe ion created by the decay of Co^{57} is stabilized to the charge state characteristic of the site which is realized at low temperatures if an Fe ion is there instead of a Co ion. But it is certain that the ordering of Fe^{2+} and Fe^{3+} is very complex below T_v . For example, the NMR spectrum was analyzed with 16 lines belonging to A sites and 32 lines belonging to B sites [11].

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