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## Analytical interpretation of temperature dependent combined quadrupolar and magnetic hyperfine interaction in $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$ (barbosalite)

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**Résumé.** — La barbosalite synthétique  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$  a été mesurée par Spectroscopie Mössbauer dans l'intervalle de température 4,2 K-295 K. Une transition magnétique a lieu à 162 K. Les spectres présentant l'interaction combinée quadrupolaire et magnétique ont été interprétés à l'aide d'une méthode analytique.

**Abstract.** — Synthetic barbosalite  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$  measured between 4.2 to 295 K by Mössbauer Spectroscopy shows a magnetic phase transition at 162 K. The spectra presenting combined quadrupolar and magnetic hyperfine interactions are interpreted using an analytical method.

**Introduction.** — We report here the study of a series of temperature-dependent Mössbauer spectra of synthetic barbosalite between 4.2 and 295 K. Below the magnetic phase transition temperature the spectra present combined magnetic-quadrupolar hyperfine interactions. This kind of spectra has been interpreted on the basis of a recalculated [1] analytical method (A.M.) first proposed by Williams and Bancroft [2].

Barbosalite,  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$  has an intriguing atomic structure [3], consisting of the packing together of iron-oxygen octahedra as triple groups and phosphate ligands. These triple groups,  $\text{Fe}^{2+}\text{-O}$  octahedron between two  $\text{Fe}^{3+}\text{-O}$  face-sharing octahedra forming isolated clusters, are linked together along the *c*-axis through the corner-shared oxygen atoms of the phosphate groups. Its synthesis as well as preliminary Mössbauer measurements have been described in a previous paper [4].

The A.M. leads to the following system of three equations with four unknowns, where the third equation is slightly different from that previously reported :

$$\sum_{\substack{i,j=1 \\ i \neq j}}^4 *E_i *E_j = a_2 = -\frac{1}{2} \left[ \frac{1}{4} (1 + \eta^2/3) \lambda^2 + 5 \right] \quad (1)$$

$$\sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^4 *E_i *E_j *E_k = -a_1 = -\frac{\lambda}{2} \times \\ \times [(1 - 2 \cos^2 \alpha - \cos^2 \gamma) \eta - 3 \cos^2 \gamma + 1] \quad (2)$$

$$*E_1 *E_2 *E_3 *E_4 = a_0 = \frac{1}{32} \times \\ \times \left\{ \frac{1}{8} (1 + \eta^2/3)^2 \lambda^4 + [(2 \cos^2 \gamma - 1) \eta^2 + \right. \\ \left. + 4(2 \cos^2 \alpha + \cos^2 \gamma - 1) \eta + (1 - 6 \cos^2 \gamma)] \lambda^2 + 18 \right\}. \quad (3)$$

The magnetic hyperfine splitting of the  $^{57}\text{Fe}$  ground state  $A_g = g_g \beta_n H$  and the reduced energy levels of the excited state,  $*E_i = E_i/A_e$  are determined from a difference table formed with the eight possible  $L_j$  spectrum lines referred to their centre of gravity,  $L_j = E_i \pm A_g/2$  ( $i = 1, \dots, 4$  and  $j = 1, \dots, 8$ ). The excited-state magnetic interaction  $A_e$  is evaluated taking the *g*-factor ratio  $g_e/g_g = -1/1.749$ . The *I.S.* and the absolute value of  $Q.S. = \frac{1}{2} e^2 qQ(1 + \eta^2/3)^{1/2}$  can be unambiguously determined from the traceless property  $\sum *E_i = 0$  and the first analytic expression respectively. The quadrupolar parameter  $B = \frac{1}{4} e^2 qQ$  and the spherical angles  $\theta$  and  $\varphi$  (determined from the direction cosines of **H** in the EFG reference frame) are functions of the asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$  which is allowed to vary in the range  $0 < \eta \leq 1$ .  $\lambda$  is the ratio between *B* and  $A_e$ .

As a check on the validity of the results we have calculated the relative intensities and the transition energies by diagonalization of the full time-independent spin Hamiltonian of the system, taking as input parameters those calculated by the A.M.

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**Results and discussions.** — Figure 1a shows the least squares fitting of the measured spectrum of synthetic barbosalite at 4.2 K. The expected two sets of hyperfine patterns, corresponding to the Fe(I) and Fe(II) systems, are indicated by four doublets per set.

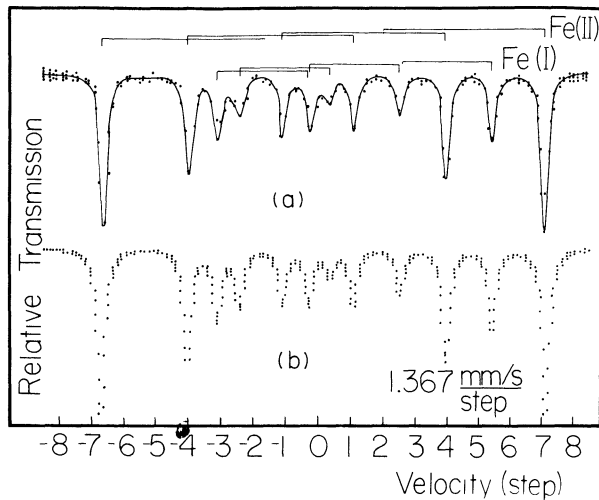


Fig. 1. — Experimental (a) and simulated (b) spectra of powder synthetic barbosalite,  $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})_2$  at 4.2 K.

This spectrum has been fitted under the following assumptions : i) Lorentzian line shape ; ii) only one line width per system. The best fit ( $\chi^2 = 1.5$ ) gives an area ratio of  $\text{Fe(II)}/\text{Fe(I)} = 2$  and 0.40 and 0.34 mm/s for the linewidth of the Fe(I) and Fe(II) sets of lines respectively.

From each set of four pairs of lines it is easy to calculate the respective spin-Hamiltonian parameters using the A.M. previously described. Table I lists these calculated values for the iron ions at the Fe(I) site for  $\eta$  varying in the range  $0 < \eta \leq 1$  in steps of 0.1. The *I.S.* and the module of *H* are unambiguously determined. The four remaining parameters *B*,  $\theta$ ,  $\varphi$  and  $\eta$  in the first octant ( $\theta, \varphi \leq \pi/2$ ) of the orthogonal

Table I. — *Mössbauer hyperfine parameters of the Fe(I) magnetic system in synthetic barbosalite at 4.2 K.*

<i>I.S.</i> (*) = 0.87 mm/s	<i>Q.S.</i> = 3.88 mm/s		<i>A<sub>g</sub></i> = 3.76 mm/s
<i>B</i> (mm/s)	$\theta$ (deg.)	$\varphi$ (deg.)	$\eta$
— 1.93	81	88	0.24
— 1.92	82	71	0.30
— 1.90	83	63	0.40
— 1.88	86	58	0.50
— 1.86	90	56	0.55

Line positions (**) (mm/s)							
Fitted :	— 5.07	— 1.31	— 4.17	— 0.41	— 1.15	2.62	2.86 6.63
Calculated :	— 5.07	— 1.30	— 4.17	— 0.41	— 1.15	2.62	2.86 6.63

Line intensities							
Fitted :	0.82	0.18	0.60	0.40	0.55	0.45	0.04 0.96
Calculated :	0.81	0.19	0.66	0.34	0.49	0.51	0.03 0.97

(\*) Relative to  $^{57}\text{Co}/\text{Pd}$  source at 4.2 K.

(\*\*) Referred to their centre of gravity.

reference frame  $V_{xx} V_{yy} V_{zz}$  span a series of correlated values within boundary limits. The intensities that appear in this table under the respective line positions are calculated by numerical diagonalization of the spin-Hamiltonian. The respective spectrum (Fig. 1b) is simulated with the same line width deduced from the experimental spectrum. It is important to note that for any of the correlated set  $B(\eta)$ ,  $\theta(\eta)$ ,  $\varphi(\eta)$ ,  $\eta$  and  $A_g$  values, the calculated line positions and intensities result the same. This fact has been already pointed out by Karyagin [5], Dabrowski *et al.* [6] and more recently by Van Dongen Torman *et al.* [7] and Ito *et al.* [8]. Nevertheless it is not yet widely recognized in the literature.

Moreover, for the Fe(I) system, the A.M. family of solutions indicates a unique sign for  $B(\eta)$  (negative). Comparison with the spectra simulated from numerical diagonalization of the spin Hamiltonian using  $+B(\eta)$  or  $-B(\eta)$  for any possible orientations of  $\mathbf{H}$ , indicates that only the negative A.M. sign fits the experimental spectra. On the other hand, it can be seen from eq. (1), (2) and (3) that the A.M. has a quadratic dependence on the angular functions. Hence, identical set of solutions for  $B(\eta)$  and  $\eta$  can be found in the remainder octants through inversions and reflections of  $\mathbf{H}$ . The full angular solution ( $0 \leq \theta \leq \pi$ ,  $0 \leq \varphi \leq 2\pi$ ) is shown in the diagram at the bottom of figure 2.

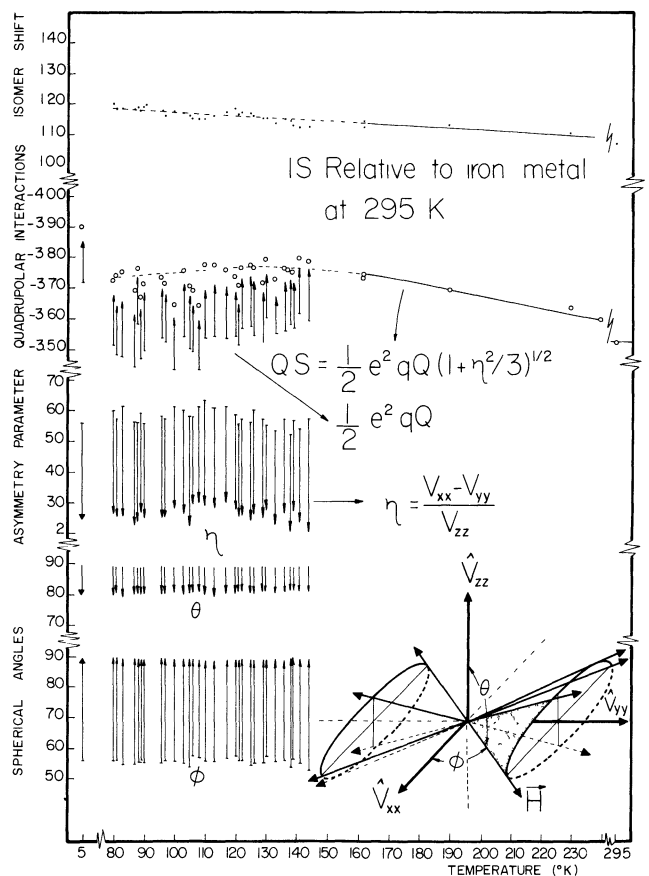


Fig. 2. — Temperature dependence of the Mössbauer parameters for the Fe(I) magnetic system. At the bottom right, the geometrical location of  $\mathbf{H}$  in the EFG reference frame.

The parameters calculated using the A.M. for the Fe(II) site at 4.2 K are given in table II. The results for the Fe(II) system must be considered with caution. For small  $\lambda$  values, the calculated parameters are strongly affected by the inaccuracy of the line position measurements. In these cases, there always exist the alternative of treating the experimental data by a perturbation method, which, usually, requires an axial symmetry assumption for the EFG tensor.

Table II. — *Mössbauer hyperfine parameters of the Fe(II) magnetic system in synthetic barbosalite at 4.2 K.*

$I.S. (*) = 0.16$ mm/s	$Q.S. = 0.60$ mm/s	$A_g = 6.97$ mm/s		
$B$ (mm/s)	$\theta$ (deg.)	$\varphi$ (deg.)	$\eta$	
$B(\eta) < 0$	-0.28 to -0.26	69 to 71	90 to 67	0.68 to 1.00
$B(\eta) > 0$	0.29 to 0.26	35 to 30	0 to 40	0.49 to 1.00

(\*) Relative to  $^{57}\text{Co}/\text{Pd}$  at 4.2 K.

From the A.M. or perturbation calculations we can deduce that for the Fe(II) system the  $I.S.$  and  $Q.S.$  parameters are not very sensitive to temperature variations in the range 4.2 K-300 K. At room temperature these parameters are both equal to  $0.40 \pm 0.02$  mm/s ( $I.S.$  relative to iron at 295 K).

Figure 2 shows the temperature dependence of the

Mössbauer parameters for the Fe(I) site, calculated by the A.M. in the first octant of the EFG reference frame. The numerical data are represented by arrows pointing toward the parameter value corresponding to the lowest  $\eta$ -value. Note that multiplication of each  $B(\eta)$  by the respective  $(1 + \eta^2/3)^{1/2}$  value gives the same  $Q.S.$  value, marked by circles in the figure.

The high and negative values of the  $Q.S.$  indicate that the ground state orbital is a  $d_z^2$  singlet and that this compound has a highly ionic character [9]. The  $d_z^2$  stabilization requires a strong trigonal distortion of the  $\text{Fe}^{2+}$ -O octahedron. The small thermal variation of the  $Q.S.$  indicates also that this orbital singlet is far apart from the next orbital and, since there is no evidence for any discontinuity up to 295 K, we can suppose that the quadrupolar sign remains unchanged up to this temperature, i.e. the  $d_z^2$  singlet remains the ground state at room temperature.

These results could be related to the strong optical-selective absorption properties of barbosalite [10]. In effect, the short Fe-Fe distance (about 2.7 Å) lies along the face-fused triplet octahedra, rendering direct electron tunneling highly likely via overlap of the  $\text{Fe}^{2+}$   $d_z^2$  orbital lobes with the  $d$ -shell of the adjacent  $\text{Fe}^{3+}$  ions. As a consequence, we can associate the  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  direction to the direction of the  $V_{zz}$  principal axis, i.e., the crystallographic direction along which the trigonal distortion stabilizes the  $d_z^2$  orbital.

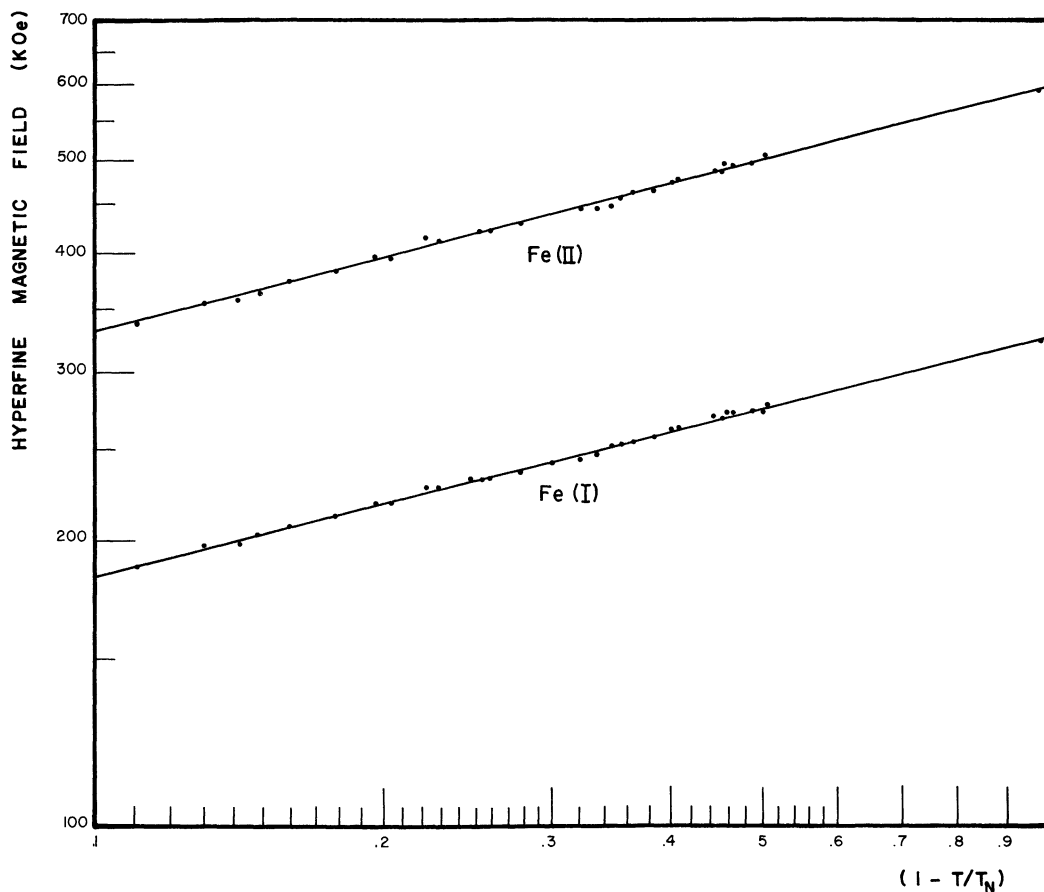


Fig. 3. — A log-log plot of the effective internal magnetic hyperfine field versus  $(1 - T/T_N)$  for the Fe(I) and Fe(II) magnetic systems. The straight lines represent a least-square fit data for  $T_N = 162$  K.

From figure 2 it can be seen that the angle  $\theta$  is relatively well defined indicating that the direction of  $\mathbf{H}$  is nearly perpendicular to the  $V_{zz}$  axis. Similar behaviour has been pointed out by Varret [11] for ferrous compounds which do not contain any other magnetically anisotropic ions and for which the energy associated with the phase transition temperature is of the same order or less than the spin-orbit coupling. This seems to be the case with barbosalite, a highly ionic compound (implying in a high orbital reduction factor) even noting that  $T_N$  is unusually high.

Another result of interest in this experiment is the temperature dependence of  $H$ . It is generally believed that the magnetic hyperfine field near  $T_N$ , the phase transition temperature, can be expressed by

$$H \propto (1 - T/T_N)^\beta$$

where  $T$  is the data-point temperature and  $\beta$  is a constant coefficient. Figure 3 is a graph of  $\ln H$  versus  $\ln(1 - T/T_N)$  for the Fe(I) and Fe(II) systems. A linear least-squares fit to all the data-points is shown.

The resulting slope of the straight-line fits for both curves is  $0.25 \pm 0.01$  and extends over the temperature range defined by

$$0.1 < (1 - T/T_N) < 1$$

where  $T_N = (162 \pm 2)$  K.

Analogous intriguing linear behaviour for temperatures far from the phase transition temperature has been reported for two iron borides [12, 13].

The experimental equality of the  $\beta$  coefficient for the Fe(I) and Fe(II) systems indicates that the  $\text{Fe}^{3+}\text{-Fe}^{2+}\text{-Fe}^{3+}$  trimer constitutes an elemental magnetic entity, as the atomic structure of barbosalite suggests.

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