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Electron paramagnetic resonance investigations of Cr³⁺ and Fe³⁺ in phases II and III of KGaF₄

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Abstract. E.P.R. studies of the Cr³⁺ ($S = 3/2$) and Fe³⁺ ($S = 5/2$) ions in the high- (II) and low- (III) temperature phases of KGaF₄ are reported. The structural phase transition close to 202 °C has been demonstrated, using the temperature dependence of the spin-Hamiltonian parameters. The main mechanism of the phase transition is driven by the rotation of the GaF₆ octahedra around the *c*-axis.

1. Introduction

The first studies [1, 2] in KGaF₄ using differential scanning calorimetry (D.S.C.) and electronic paramagnetic resonance (E.P.R.) experiments revealed a structural phase transition at high temperature (in the vicinity of 200 °C). The superposition model [3] was also successfully tested for the room temperature phase.

In this paper, preliminary studies of the critical behaviour of KGaF₄ using an E.P.R. technique for single crystals are described. Our purpose is to study the influence of the Cr³⁺ or Fe³⁺ E.P.R. probe diluted in the host lattice of KGaF₄, and to present the temperature dependence of the spin-Hamiltonian parameters on both sides of the transition (for the Cr³⁺ case).

2. Structural description

The KMF₄ (M = Ga, Fe, Ti or V) layered compounds have been the subject of many investigations. Their structures, displayed in figure 1(a), consist of two-dimensional (2D) networks of MF₆ octahedra separated by layers of potassium ions [4]. The octahedra layer at the coordinate *c*/2 is translated by *b*/2. The symmetry of the aristotype phase (called phase I) is orthorhombic, space group *Ammm*. These compounds exhibit a structural transition between the so-called phase II (high temperature) and a low-temperature phase (phase III, space group *Pmcn*). In KGaF₄, the transition temperature is close to 202 °C.

In the case of KFeF₄, the structures of both phase II (space group *Amma*) and phase III have been fully reported [5, 6]. For KGaF₄, the structure of the room temperature phase, determined using single-crystal x-ray diffraction data [1], is shown in figure 1(b). Until now, structure determination of the high-temperature phase II using x-ray powder diffraction techniques has proved to be unsuccessful [7] owing to a very strong preferred orientation. Nevertheless, all the peaks in the pattern could be indexed in the same space group *Amma* as for KFeF₄ (phase II), thus showing the isotype character of KGaF₄ and this

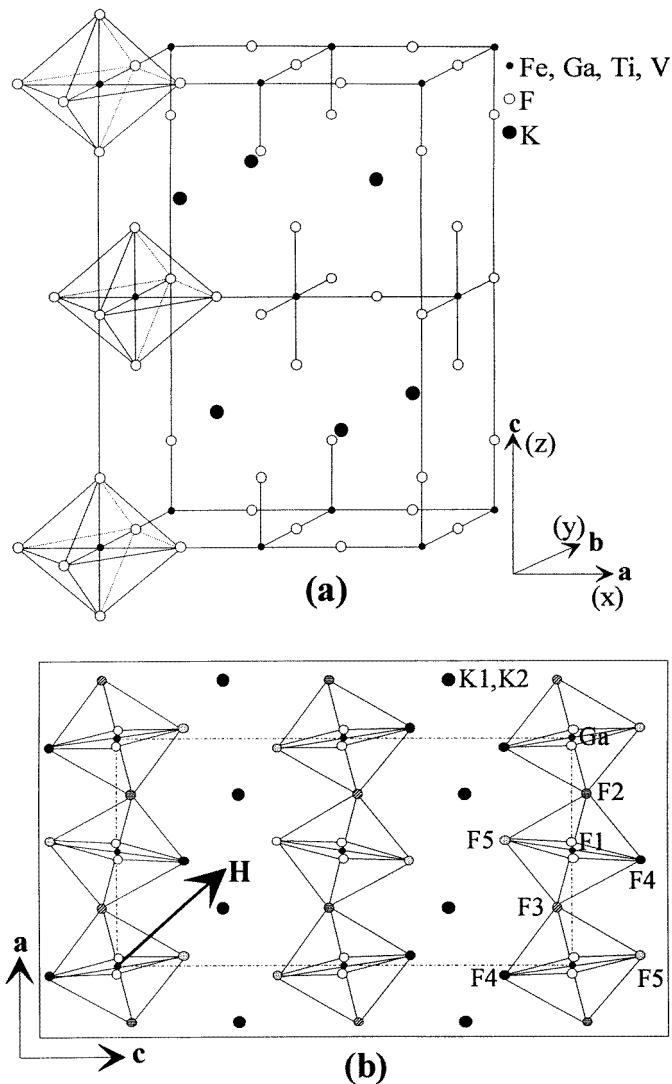


Figure 1. (a) The aristotype phase (called phase I) of the structural family of the KMF_4 series ($M = Fe, Ga, Ti$ or V). (b) $KGaF_4$ in phase III; a projection of the structure onto the (010) plane. In this plane there are two inequivalent 'orientations' (four sites equivalent in pairs) of GaF_6 octahedra as regards the magnetic field (H) and two systems of lines are observed in the spectra (see figure 3).

latter compound. In phase II, both fluorines F1 (figure 1(b)) are aligned along the b -axis, while the fluorines F2 and F4 become equivalent to F3 and F5 respectively.

3. Experimental procedures

$KGaF_4$ single crystals were grown using a chloride flux technique [8]. For E.P.R. experiments, chromium chloride or iron fluoride was added to the growth mixture in

amounts corresponding to a molar ratio M³⁺/Ga³⁺ (M = Cr or Fe) of 1% to 2%.

The E.P.R. spectra were recorded on a conventional Bruker X-band spectrometer (3 cm, 9.75 GHz). The static magnetic field may be varied in the range 0–10 500 G. The temperature dependence was studied in the range 20–250 °C using a gas circulation system. The temperature stability was ensured by the high inertia of our home-made system.

4. E.P.R. investigations

4.1. Theory

E.P.R. investigations consist in the determination of magnetic axes of (CrF₆)³⁻ and (FeF₆)³⁻ complexes in KGaF₄:Cr³⁺ and KGaF₄:Fe³⁺, of spin-Hamiltonian parameters and of the angular dependence of the line positions. The Cr³⁺ (*S* = 3/2) or Fe³⁺ (*S* = 5/2) paramagnetic probe is substituted for a Ga³⁺ ion located at the centre of the fluorine octahedra in GaF₆. The lattice relaxation around the impurity should be very small because of the very close values of the ionic radii of Fe³⁺ (0.64 Å), Cr³⁺ (0.63 Å) and Ga³⁺ (0.62 Å).

The spin Hamiltonian of the Fe³⁺ ion in phase II is given by

$$\mathcal{H} = \beta(g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) + \frac{1}{3}(b_2^0 O_2^0 \pm b_2^1 O_2^1 + b_2^2 O_2^2) + \frac{1}{60}(b_4^0 O_4^0 \pm b_4^1 O_4^1 + b_4^2 O_4^2 \pm b_4^3 O_4^3 + b_4^4 O_4^4) \quad (1)$$

where the first term accounts for the Zeeman interaction. The remaining terms are associated with crystal-field interactions due to the probe surroundings (for the Cr³⁺ ion, fourth-order parameters are not allowed). The O_n^m and b_n^m are the Stevens tensorial operators and the crystal-field parameters respectively. In phase II, the probe site symmetry is 2/*m* which justifies the presence of b_n^m with odd values of *m*. The b_n^m -terms with even *m* and *m* ≠ 0 are related to the distortion of equatorial bonds (Ga–F_{*i*}, *i* = 1, 2, 3, 4). The ± sign results from the transformation of O_n^m -operators by the point group symmetry operations. The principal axes *x*, *y* and *z* are chosen as shown in figure 1(a). According to this choice, the *z*-axis direction is close to the shortest direction of the probe–fluorine bond and the spin-Hamiltonian parameters are determined in this frame.

In the low-temperature phase (III), the probe site symmetry is 1 (*C*₁) which allows $b_n^m O_n^m$ -terms with *m* < 0.

4.2. Experimental results

The spin-Hamiltonian parameter determination is not trivial. Owing to the large number of crystallographic sites for M³⁺/Ga³⁺ in the unit cell (four for phase II and eight for phase III; see figures 1(b) and 2), to the superhyperfine interaction (the Fe³⁺ case), and to fine-structure transitions which do not obey the normal selection rule, the E.P.R. spectra are complicated. In order to indicate the lines, the energy levels for Fe³⁺ are labelled *k* = 6 to 1 (*k* = 4 to 1 for Cr³⁺) and the transitions are labelled with letters: A to E if *k* → *k* – 1, F to I if *k* → *k* – 2, J to L if *k* → *k* – 3, ... (A to C if *k* → *k* – 1 etc in the case of Cr³⁺).

In a first step, the orientation of the magnetic axes was deduced from the experimental spectra and refined using the spin-Hamiltonian parameters (figure 2). Their directions correspond to the largest splitting observed in the spectra. Indeed the contribution of the term b_2^0 (and b_4^0 for the Fe³⁺ case) is maximal when the magnetic field is along a probe–fluorine bond. It is worth noting that two sets of lines will be observed in any plane in the low-temperature phase (III), whereas in phase II they will be observed only in the (010) plane.

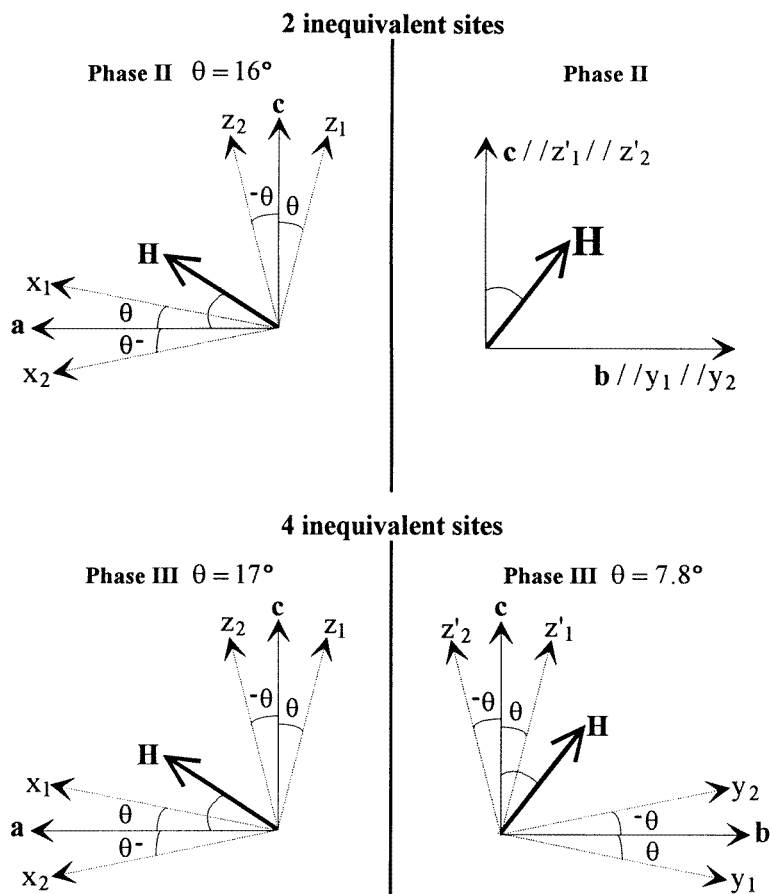


Figure 2. Projections of the magnetic axes ($x_i, y_i, z_i, z'_i, i = 1, 2$) onto the plane. The Cr^{3+} -ion angular values are indicated.

In phase II, when the magnetic field (H) belongs to the (010) plane, the lines are split owing to the non-diagonal terms b_n^m (with odd m), whose large values allow transitions with $\Delta k = \pm 2$: E1 and E2 for the Cr^{3+} case (figure 3) or H1 and H2 for the Fe^{3+} case (figure 4) for example.

In phase III the additional terms b_n^m with $m < 0$ split the lines when H is aligned in (100) or (001) planes (figure 4). The coincidences of the lines occur when H is along the a -, b - or c -axis.

Table 1. Spin-Hamiltonian parameters at 220 °C for the Cr^{3+} ($S = 3/2$) ion in phase II. The b_n^m are given in units of 10^{-4} cm^{-1} . The second inequivalent sites are obtained by reversing the sign of b_2^1 .

g_z	g_x	g_y	b_2^0	b_2^1	b_2^2
1.965 ± 0.002	1.978 ± 0.002	1.978 ± 0.002	1711 ± 2	2949 ± 5	469 ± 2

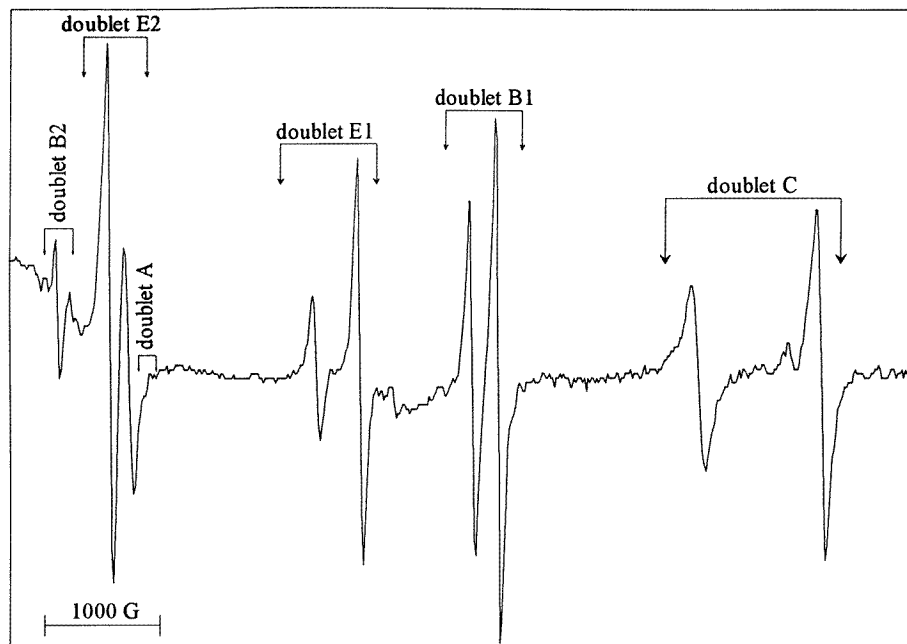


Figure 3. The E.P.R. spectrum of KGaF₄:Cr³⁺ in phase II, for rotation around the *b*-axis. $\theta = (\mathbf{H}, \mathbf{c}) = \pm 4^\circ$.

Table 2. Spin-Hamiltonian parameters at 235 °C for the Fe³⁺ ($S = 5/2$) ion in phase II. The b_n^m are given in units of 10^{-4} cm^{-1} . The second inequivalent sites are obtained by reversing the signs of b_2^1 , b_4^1 and b_4^3 .

g_z	g_x	g_y	b_2^0	b_2^1	b_2^2
2.0023	2.0035	2.0035	1480 ± 1	1855 ± 5	435 ± 2
b_4^0	b_4^1	b_4^2	b_4^3	b_4^4	
-18.3 ± 1.0	-93 ± 5	-23 ± 4	50 ± 5	-38 ± 5	

Table 3. Spin-Hamiltonian parameters at room temperature for the Cr³⁺ ($S = 3/2$) ion in phase III. The b_n^m are given in units of 10^{-4} cm^{-1} .

	g_z	g_x	g_y	
	1.965 ± 0.002	1.983 ± 0.004	1.965 ± 0.004	
b_2^{-2}	b_2^{-1}	b_2^0	b_2^1	b_2^2
217.3 ± 10.0	-1453 ± 10	1585.2 ± 2.0	-2920 ± 5	464 ± 2

In order to determine the spin-Hamiltonian parameters, line positions were measured for different magnetic field orientations in the (100), (010) and (001) planes. The angular dependences of E.P.R. line positions are shown in figures 5 and 6. The spin-Hamiltonian

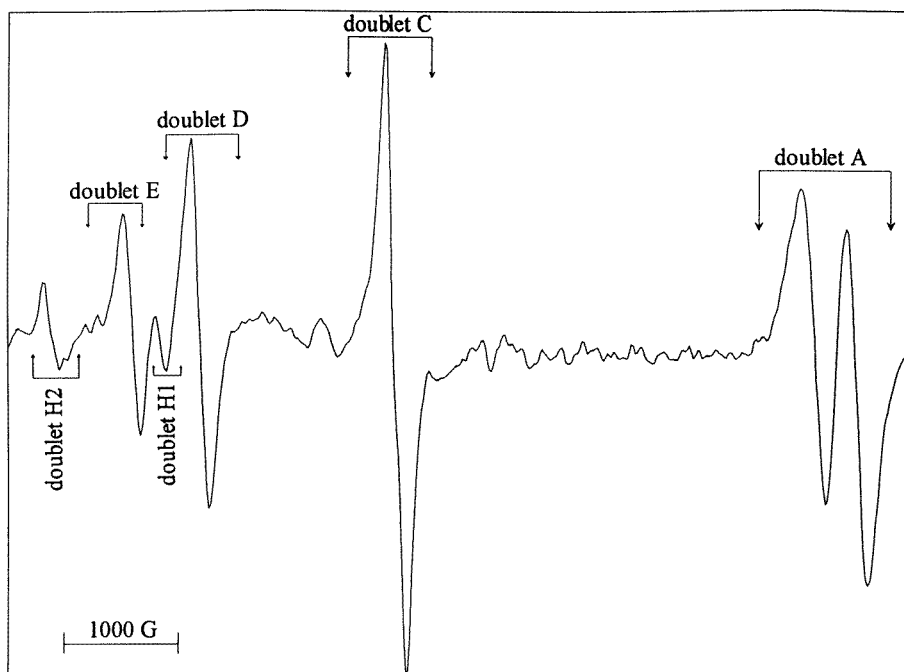


Figure 4. The E.P.R. spectrum for the Fe^{3+} ion in phase III of KGaF_4 , for rotation around the c -axis. $\theta = (\mathbf{H}, \mathbf{b}) = \pm 15^\circ$. Unlike in the case of the Cr^{3+} ion, the iron lines are very broad; this is due to the unresolved superhyperfine structure.

Table 4. Spin-Hamiltonian parameters at room temperature for the Fe^{3+} ($S = 5/2$) ion in phase III. The b_n^m are given in units of 10^{-4} cm^{-1} .

g_z	g_x	g_y	b_2^{-2}	b_2^{-1}	b_2^0	b_2^1	b_2^2	
2.0023	2.0035	2.0035	83 ± 2	83 ± 5	1518 ± 1	2051 ± 5	459 ± 2	
b_4^{-4}	b_4^{-3}	b_4^{-2}	b_4^{-1}	b_4^0	b_4^1	b_4^2	b_4^3	b_4^4
10 ± 5	-87 ± 5	-16 ± 4	33 ± 5	-12.4 ± 1.0	-97 ± 5	59 ± 4	-87 ± 5	-5 ± 5

parameters have been refined by successive adjustments. The computer program used is able to calculate line positions after diagonalizing the spin Hamiltonian for each angle between \mathbf{H} and the principal axes. In order to obtain the best agreement between experimental and calculated positions, comparisons have been made using six different orientations in each one of the planes (100), (010) and (001).

The results are listed in tables 1 to 4. They account for all details of the experimental spectra accurately. Knowledge of the spin-Hamiltonian parameters enables the angular dependence to be plotted (figures 5 and 6) and the good agreement with the experimental positions to be verified. These curves are conformable to the structural model considered and reflect correctly the symmetry elements and the number of inequivalent sites.

In addition, the spin-Hamiltonian parameters allow one to calculate the energy levels

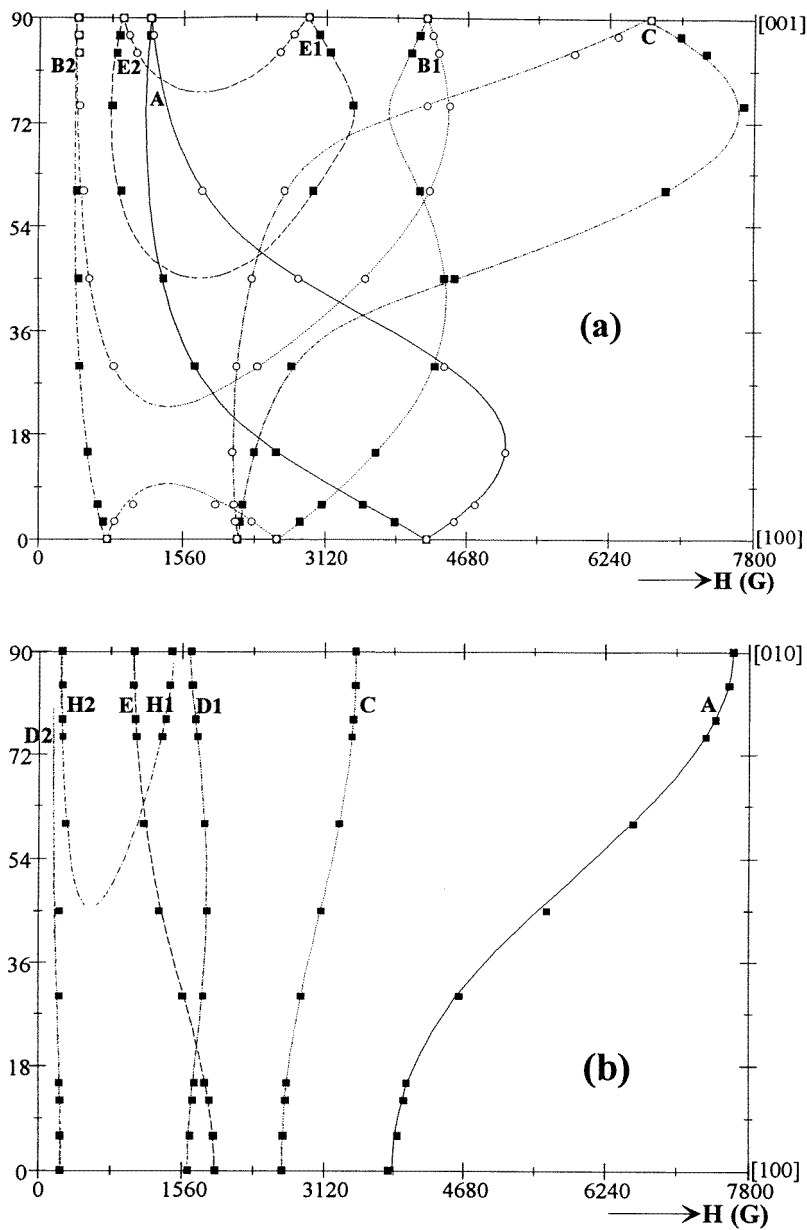


Figure 5. E.P.R. line positions for Cr^{3+} (a) and Fe^{3+} (b) ions in the high-temperature phase (II) of $KGaF_4$ when H rotates in the (010) plane (a) and in the (001) plane (b). The symbols \blacksquare and \circ correspond to the two inequivalent sites. The continued and dashed lines correspond to the positions calculated using the spin-Hamiltonian parameters. In the (001) and (100) planes all of the four sites are equivalent, while they are equivalent in pairs in the (010) plane (see again figure 2).

and then to plot energy diagrams (figure 7). These latter show that the B transitions (B1 and B2) are situated on nearly flat energy levels when the magnetic field is (i) in the (001) plane

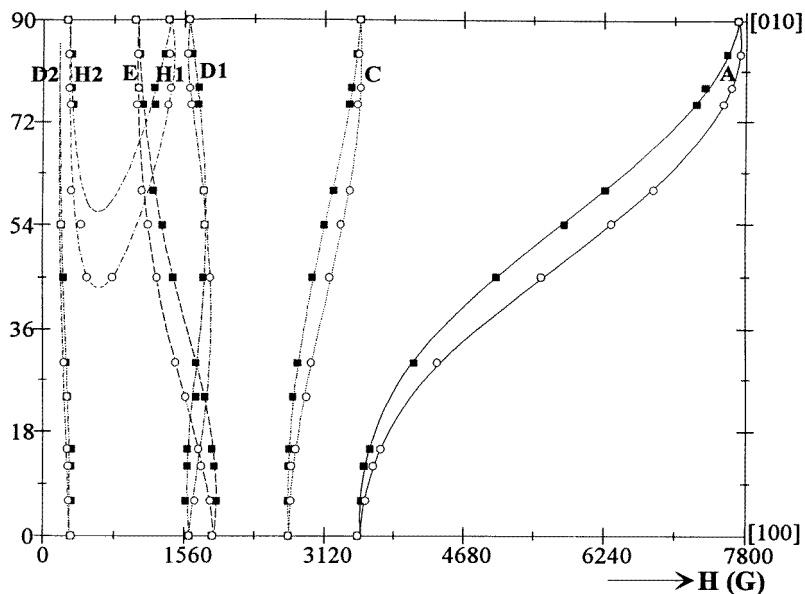


Figure 6. The angular dependence of the line positions of the Fe^{3+} ion in phase III of KGaF_4 , for rotation around c -axis. The symbols \blacksquare and \circ correspond to the two inequivalent sites. The continued and dashed lines correspond to the positions calculated using the spin-Hamiltonian parameters. In the (100), (010) and (001) planes, the eight sites are equivalent in fours (see again figure 2).

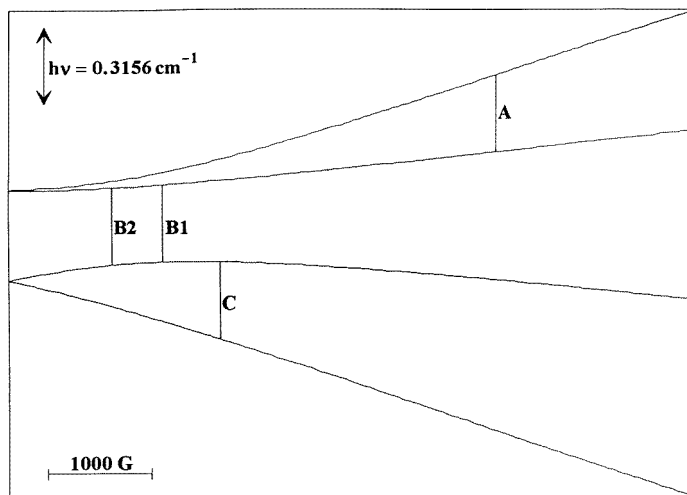


Figure 7. Energy levels of $\text{KGaF}_4:\text{Cr}^{3+}$ in phase III (ν is the E.P.R. frequency), for rotation around the b -axis. $\theta = (\mathbf{H}, \mathbf{a}) = 20^\circ$ (for the second inequivalent site in the (010) plane). The observed transitions are indicated.

and (ii) along particular orientations in the (010) plane (figure 7). A slight modification of the site symmetry or of the energy of these levels yields a large shifting of line positions. In

phase II, for some orientations, these transitions are totally absent (figure 5). Their presence in phase III is related to the symmetry change (i.e. to the phase transition). However, these transitions are observed with the K-band frequency (≈ 1.55 cm, 19.3 GHz).

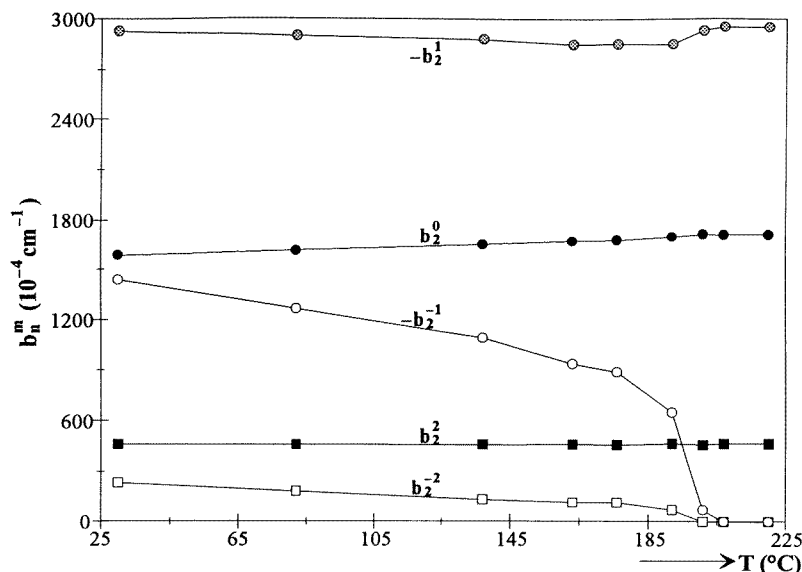


Figure 8. The behaviour of the spin-Hamiltonian parameters for the Cr³⁺ ion in KGaF₄ as a function of the temperature. This figure clearly shows that only b_2^{-2} and b_2^{-1} reflect the mechanisms of the phase transition. The other terms are practically constant.

In order to determine the contribution of different spin-Hamiltonian parameters to the critical phenomena and to evaluate the temperature of the phase II \rightarrow phase III transition, a study from room temperature up to 220 °C for these parameters has been realized (figure 8). Our results clearly show that only the b_n^m -terms with $m < 0$ reflect the mechanisms of the phase transition. Indeed from $T = 192$ °C, these latter decrease swiftly and become zero at $T = 201$ °C for b_2^{-2} and at $T = 207$ °C for b_2^{-1} (the Cr³⁺ case). The contribution of other terms is insignificant. This study leads to the result that the temperature of the phase transition is equal to $T_c \cong 202$ °C.

5. Discussion and conclusion

E.P.R. results for phases II and III of KGaF₄ have been fully reported. The great sensitivity of the lines to the orientation of the magnetic field allows us to account for the symmetry elements of each phase. Fe³⁺ lines are generally broad and the determination of b_n^m is less precise; however, Cr³⁺ and Fe³⁺ ions constitute good probes in the host lattice of KGaF₄.

This study shows that measurements on paramagnetic local probes allow one to describe correctly the first-order effect of the symmetry breaking. As a matter of fact, as long as the b_n^m -terms with $m < 0$ can be expressed as functions of the angle (ϕ_c) of the rotation of the GaF₆ octahedra around the c -axis:

$$b_2^{-2} = -b_2^2|_{\text{II}} \sin(2\phi_c) \quad b_2^{-1} = -b_2^1|_{\text{II}} \sin(\phi_c)$$

where $b_2^2|_{\text{II}}$ and $b_2^1|_{\text{II}}$ are the high-temperature phase parameters (for the Fe^{3+} case, the four order parameters must be added), the angle ϕ_c is a good approximation to the amplitude of the order parameter of the phase II \rightarrow phase III transition. Therefore, the behaviour of the b_n^m as functions of the temperature (see figure 8) allows one to conclude that there is a small tilting of the octahedra, typically $\phi_c \cong 8^\circ$ [7]. The critical behaviour obtained using the E.P.R. technique and single-crystal x-ray diffraction will be published in a forthcoming paper.

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