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# Electron paramagnetic resonance and x-ray studies of the critical behaviour of the $KGaF_4$ layered compound

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**Abstract.** Detailed EPR and x-ray studies of the static critical behaviour in $KGaF_4$ are reported. All measurements were performed on single crystals. Dilatometric experiments have allowed us to characterize the II $\rightarrow$ III phase transition. It is accompanied by a contraction of the $a$ and $b$ parameters, which is consistent with a rotation of the $GaF_6$ octahedra around the $c$ axis, and by an anomaly along the $c$ direction. The first-order character of the structural phase transition has been demonstrated using EPR and diffractometric measurements. DSC experiments have allowed us to conclude that this discontinuity is weak. In addition, the interpretation of the phase transition in the continuous or quasi-continuous approach (i.e. $\beta = 0.140 \pm 0.006$ for $0.10 \times 10^{-4} \leqslant t < 10.53 \times 10^{-2}$ and $T_C = 201.83\,^{\circ}\mathrm{C}$) has allowed us to conclude that this latter is essentially of a 2D character.

## 1. Introduction

There have been many investigations of the $KMF_4$ layered compounds, particularly on $KFeF_4$. These compounds exhibit at high temperature (very close to 202 °C for the $KGaF_4$ case) a structural phase transition between the so-called phase II (high temperature, space group $Amma$) and phase III (low temperature, space group $Pmcn$).

In this paper we are interested in $KGaF_4$. The first studies [1, 2] of this compound using differential scanning calorimetry (DSC), electron paramagnetic resonance (EPR) and Raman scattering have allowed us to detect the transition. According to our previous EPR study [3] the main mechanism of the phase transition is driven by the rotations of the $GaF_6$ octahedra around the $c$ axis (figure 1). Our purpose is to use a local technique (EPR) and a long-range technique (x-ray) for a single crystal to describe the critical behaviour of $KGaF_4$ at the phase transition II $\rightarrow$ III. Many studies in the $KFeF_4$ isotype compound have shown that the mechanisms of the phase transition are complex. Indeed, according to Bianchi *et al* [4] an intermediate modulated phase between the phase II and the phase III is possible. Furthermore, the recent studies on this latter compound have shown that the phase transition II $\rightarrow$ III is quasi-continuous or it is weak to first order [5]. According to precise studies [6] the possibility of a double transition in a small temperature range is not excluded. In this work we want to prove through $KGaF_4$ the discontinuous character of the phase transition II $\rightarrow$ III, and to show that this phase transition is essentially of a (two-dimensional) 2D nature. These conclusions are derived from a careful analysis of the EPR spectra and the x-ray patterns in the critical region. Indeed, between the temperature

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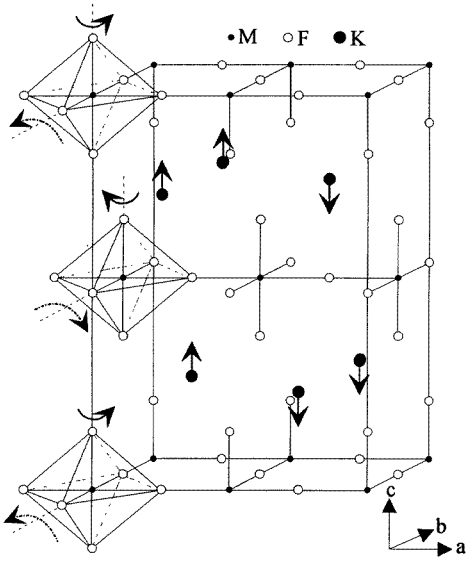


**Figure 1.** The arisotype phase (called phase I, space group *Ammm*) of the structural family of the $KMF_4$ series (M = Fe, Ga, Ti or Vi). For clarity reasons only a few $MF_6$ octahedra are shown. Arrows indicate the shift of the potassium ions (vertical arrows) and the tilting of the octahedra at the transition I → II (dashed arrows) and at the transition II → III (continuous arrows).

where the sample is clearly in phase II or in phase III, the analysis of the shape of the lines allowed us to conclude the existence of a small temperature range in which the disordered phase and cluster phenomena are observed. In addition, the intensity of the superstructure reflections just above the transition temperature $T_C$ is non-zero, but vanishes only 10 °C or more above. Furthermore, the discontinuity in the order parameter at the transition is non-insignificant.

The organization of this paper is as follows. After a brief presentation of experimental procedures, dilatometric measurements are presented to characterize the phase transition II → III. The evolution of the cell parameters as a function of temperature is a good complement to the comprehension of the mechanism of the phase transition and has confirmed the complexity of this transition. In section 4, EPR measurements—using $Cr^{3+}$ and $Fe^{3+}$ probes—in the critical region are given. Then, in the continuous or quasi-continuous approach, a precise determination of the critical exponent $\beta$ allows to conclude that the phase transition II → III belongs to the 2D Ising model. Finally, to account for spectra in the vicinity of $T_C$, the Landau theory of first-order transitions has been applied. In the last section, we shall use the diffractometric measurements to confirm the discontinuous character of the transition. DSC measurements have allowed us to conclude that this discontinuity of the structural phase transition II → III is weak.

## 2. Experimental procedures

$KGaF_4$ single crystals were grown using a chloride flux technique [7]. For EPR experiments, chromium chloride or iron fluoride was added to the growth mixture in amounts corresponding to a molar ratio $M^{3+}/Ga^{3+}$ (M = Cr or Fe) of 1–2%.

The EPR spectra were recorded on a conventional Bruker X-band spectrometer (3 cm, 9.75 GHz). The static magnetic field was 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 (0.05 °C) was ensured by the high inertia of our home-made system; with this system the accuracy on the temperature measurements is less than 0.1 °C.

X-ray single-crystal patterns were recorded with Cu K$\alpha$ radiation using a rotating anode on a high-accuracy goniometer ($\Delta\theta = 2 \times 10^{-4}$ °). For the temperature studies, the sample was placed in a Rigaku furnace which allows a temperature stability of 0.1 °C. The patterns were recorded from room temperature up to 270 °C.

## 3. Dilatometric study of a $KGaF_4$ single crystal

Lattice parameters were calculated by adjustment of the peaks (reflections 800 for the *a* parameter, 080 for the *b* and 0014 for the *c* parameter) at each temperature. Their evolution as a function of temperature from room temperature up to 270 °C is given in figure 2. These curves clearly exhibit two kinds of behaviour.

(i) We observe a regular and linear dependence of the cell parameters from room temperature up to 177 °C for phase III and from 210 °C for phase II, which can be approximated with a good accuracy by the following relations:

$$a_{II} = 7.4940 + 2.1295 \times 10^{-4}T \qquad 2b_{II} = 7.6559 + 1.3301 \times 10^{-4}T$$
$$c_{II} = 12.1811 + 3.5168 \times 10^{-4}T$$
$$a_{III} = 7.4823 + 2.3402 \times 0^{-4}T \qquad b_{III} = 7.6296 + 2.0815 \times 10^{-4}T$$
$$c_{III} = 12.2125 + 2.5739 \times 10^{-4}T.$$

Owing to the decomposition of the crystal, the latter cannot be heated above 275 °C.

(ii) Between 177 and 210 °C, the behaviour of the three parameters is more or less complex. The evolution of the *a* and *b* parameters is similar. Nevertheless, the contraction of the cell along the *a* axis is quasi-continuous (according to the studies in the $KFeF_4$ isotype compound [5], this is related to the initial rotation of the octahedra around the *b* axis, figure 1). In the non-distorting-and-rigid-octahedron model, the evolution of the cell parameters in this temperature range is consistent with a rotation of the $GaF_6$ octahedra around the *c* axis. As far as the *c* parameter is concerned, when the sample is cooled, the rotation around the *c* axis allows a small vertical repulsion of the potassium ions. Indeed, they are located at the centre of the $GaF_6$ octahedron cages (figure 1). Therefore, the *c* parameter must increase from phase II to phase III, which is in good agreement with figure 2.

The transition temperature corresponds to the temperature where the evolution curve of each parameter presents one inflection point. For the three parameters, $T_C$ is very close to 202 °C. The divergence of the linewidth of the reflections associated with the *a* and *b* parameters has been observed at the transition, whereas the linewidth of the reflection associated with the *c* parameter remains practically constant.

Our results are in close agreement with the dilatometric study of the $KFeF_4$ isotype compound [5]. Nevertheless, a splitting of the reflections (080 for example) above $T_C$ up to 10 °C (or 12 °C) above the transition has been observed. This will be discussed in section 5.

## 4. EPR results and critical behaviour

According to the previous studies [3] and to the dilatometric results, the main mechanism of the phase transition in $KGaF_4$ is driven by the rotations of the $GaF_6$ octahedra around

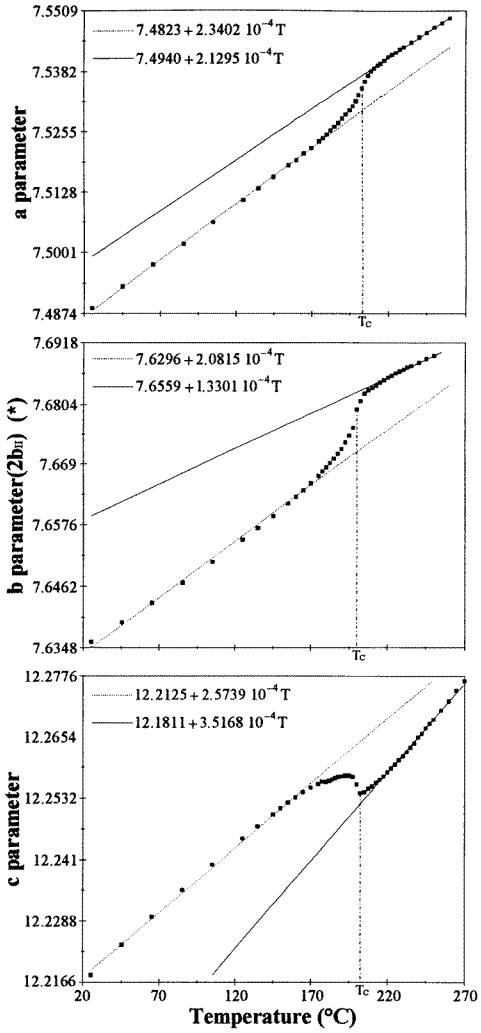


**Figure 2.** Evolution of the lattice parameters (Å) of $KGaF_4$ as a function of temperature. $*$ indicates that the phase transition II $\rightarrow$ III is accompanied by an increase of the $b$ parameter by a factor of two.

the $c$ axis. Therefore, if $\phi_c$ is the tilt of the octahedra, the phase transition II $\rightarrow$ III can be described by the Hamiltonian

$$H(\phi_c) = \beta \boldsymbol{H}\, \tilde{g}\, \boldsymbol{S} + \tfrac{1}{3}\left(b_2^0 O_2^0 \pm b_2^1 O_2^1 + b_2^2 O_2^2\right) + \Delta H(\phi_c)$$

where the first term accounts for the Zeeman interaction. The second term is the crystal-field Hamiltonian for the high-symmetry phase (phase II). For the $Fe^{3+}$ probe, the fourth-order terms must be added. The values of spin-Hamiltonian parameters at 220 °C (phase II) for the $Cr^{3+}$ probe are the following [3]:

$$g_x = g_y = 1.978 \pm 0.002 \qquad g_z = 1.965 \pm 0.002$$
$$b_2^0 = 1711 \pm 2 \qquad b_2^1 = 2949 \pm 5 \qquad b_2^2 = 469 \pm 2$$

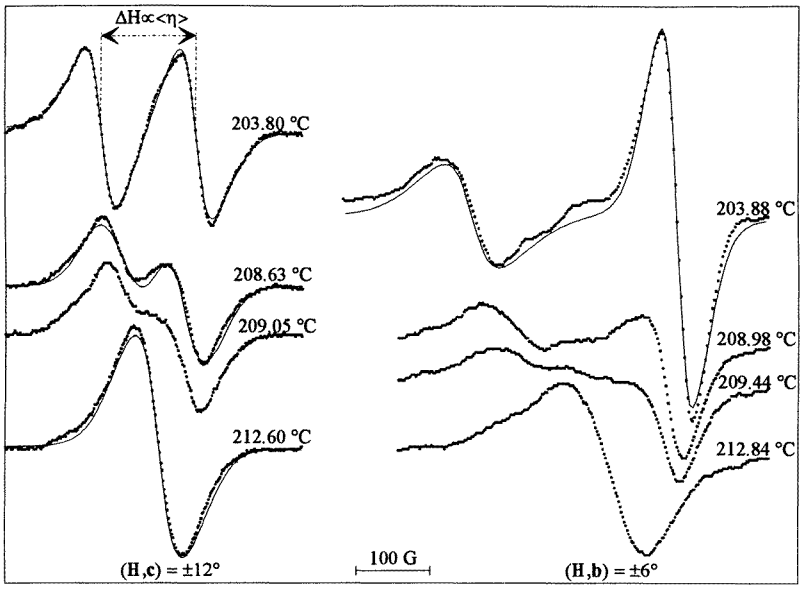


**Figure 3.** EPR spectra of $KGaF_4$:$Cr^{3+}$ for rotation around the $a$ axis (the continuous line is the reconstruction): evolution of the shape of the lines in the vicinity of $T_C$ (left-hand side, $1/2 \leftrightarrow -1/2$ transition; right-hand side, $3/2 \leftrightarrow 1/2$ transition).

(the $b_2^m$ are given in units of $10^{-4}$ $cm^{-1}$). As far as the $\Delta H(\phi_c)$ Hamiltonian is concerned

$$\Delta H(\phi_c) = -\frac{1}{3}\left[b_2^1 O_2^{-1}\sin(\phi_c) + b_2^2 O_2^{-2}\sin(2\phi_c)\right] + \frac{1}{3}\sum_{m=0}^{2}\left(\delta b_2^m\right) O_2^m$$

(with $\delta b_2^0 = 13.5 \pm 2.0$, $\delta b_2^1 = 100 \pm 5$, $\delta b_2^2 = 1 \pm 2$ at 192 °C), the first term allows us to describe the first-order effect of the symmetry breaking in the critical region. The second term accounts for the fluctuations of the crystal-field Hamiltonian of phase II. Therefore, the angle $\phi_c$ is a good approximation to the amplitude of the order parameter of the structural phase transition II $\rightarrow$ III.

In the EPR technique, the shift of the resonance field and, more precisely, the splitting of the line (figures 3 and 4) is directly related to the order parameter

$$\Delta H(\phi_c) = \alpha_1(\theta) b_2^1 \sin(\phi_c) + \alpha_2(\theta) b_2^2 \sin(2\phi_c) + \ldots$$

where $\theta$ is the orientation of the static magnetic field. The $\alpha_i$ coefficients have been determinated by numerical calculations. For the $Cr^{3+}$ probe, their values for $\theta = (\boldsymbol{H}, \boldsymbol{b}) = \pm 6^\circ$ in the (100) plane and for the $3/2 \leftrightarrow 1/2$ transition are $\alpha_1 = -0.450$ and $\alpha_2 = 0.124$. In this plane, only the first-order effects of the symmetry breaking are observed. The reconstruction of the EPR spectrum by the discrete lines at each temperature allows us to measure the resonance fields. Their evolution versus temperature is given in figure 4. In the vicinity of $T_C$, the reconstruction of the EPR spectra by two or one discrete lines has proved to be unsuccessful owing to the particular shape of the lines (figure 3). However, in the temperature range indicated by (1) in figure 4(a), it is always possible to account for the spectrum using three discrete lines (see figure 6(a) for example). These problems arise for many directions of the magnetic static field, but in this work only the directions where

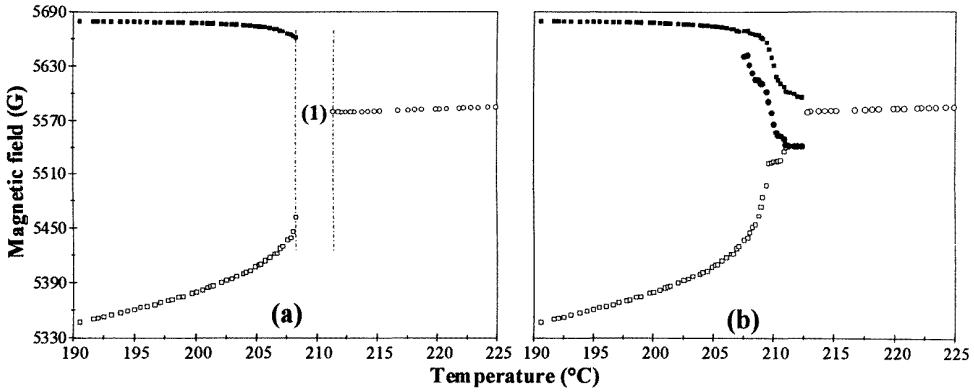


**Figure 4.** Line positions (for the $Cr^{3+}$ case) of the $3/2 \leftrightarrow 1/2$ transition versus the temperature for rotation around the $a$ axis $(\boldsymbol{H}, \boldsymbol{b}) = \pm 6^{\circ}$. (a) Continuous or quasi-continuous approach: reconstruction of the EPR spectrum by two (phase III) or by one (phase II) discrete lines (see again figure 3). In the temperature range indicated by (1), the reconstruction is not possible. (b) Discontinuous approach: reconstruction by three discrete lines in the critical region (see again figure 6).

the maximum sensitivity at the phase transition occurs have been chosen. Therefore, to determine the nature of the phase transition in $KGaF_4$, two hypotheses can be considered.

### *4.1. The continuous approach*

Insofar as the temperature range indicated by (1) in figure 4(a) is quite small ($\approx 3.2\,^{\circ}C$), the shape of the lines close to $T_C$ can be related to critical fluctuations or to precursor phenomena. Indeed, we have a good agreement by the adjustment of the order parameter with a critical law $\langle \eta \rangle \propto (T_C - T)^{\beta}$

$$1.58 \times 10^{-3} \leqslant t \leqslant 8.76 \times 10^{-2} \quad \beta = 0.139 \pm 0.005 \quad \text{for } Cr^{3+} \text{ probe}$$
$$1.10 \times 10^{-4} \leqslant t < 10.53 \times 10^{-2} \quad \beta = 0.140 \pm 0.006 \quad \text{for } Fe^{3+} \text{ probe}$$
$$\text{with } t = \frac{T_C - T}{T_C}.$$

These results are obtained for many directions of the magnetic field, but for the above reasons only two directions are reported in figure 5. For the $Cr^{3+}$ case, temperatures values are shifted with regard to the real values; this is due to the fact that our measures do not give an absolute value of temperature. According to the critical exponent, the phase transition belongs to the Ising universality class $d = 2$, $n = 1$. In addition, our results are in agreement with the Mössbauer studies of the $KFeF_4$ isotype compound ($\beta = 0.151$) [8]. A similar value of $\beta$ has been obtained in other bidimensional systems such as $K_2NiF_4$ ($\beta = 0.138$), $K_2MnF_4$ ($\beta = 0.15$), $Rb_2MnF_4$ ($\beta = 0.16$), $(CH_3NH_3)_2FeCl_4$ ($\beta = 0.146$) [9].

However, near the transition temperature the splitting of the lines does not go to zero, but rather remains very important up to 150 G for some orientations of the static magnetic field, whereas the maximum linewidth does not exceed 60 G. Therefore, it cannot be ascribed to the linewidth broadening effect. This suggests a first-order character of the transition.

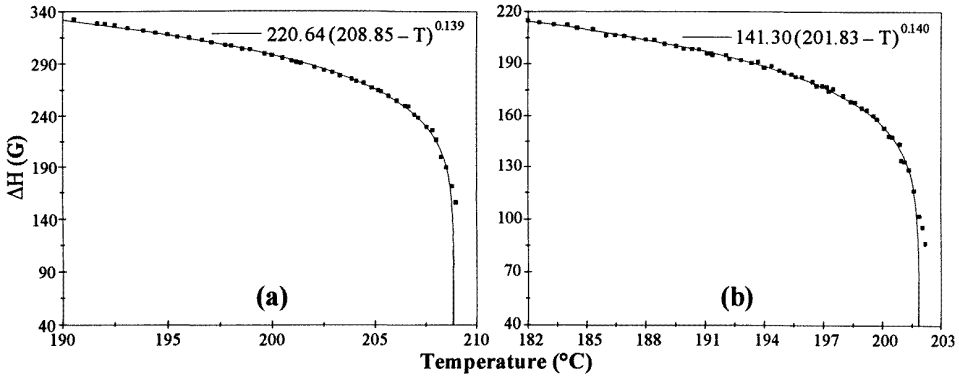


**Figure 5.** The $\beta$ critical exponent measured by fitting the splitting of the line versus the temperature with a critical law $\Delta H_0\,(T_C - T)^{\beta}$. (a) $Cr^{3+}$ probe, $\beta = 0.139 \pm 0.005$, for the $3/2 \leftrightarrow 1/2$ transition; (b) $Fe^{3+}$ probe, $\beta = 0.140 \pm 0.006$, for the $5/2 \leftrightarrow 3/2$ transition.

### *4.2. Coexistence of phases*

To account for spectra in the vicinity of $T_C$, the hypothesis of the discontinuous transition with coexistence of phases has been considered. The small value of $\beta$ is in agreement with a first-order character of the phase transition II $\rightarrow$ III. The coexistence of phases in the EPR spectra is described by the superposition of two low-temperature components and one high-temperature component. The example of the reconstruction for $T - T_C = 2\,^{\circ}\mathrm{C}$ is reported in figure 6(a), and the evolution versus the temperature of the corresponding line positions is shown in figure 4(b). The problem has been to determine the temperature where the reconstruction using three discrete lines is better than that using two discrete lines. In addition, we have observed that the intensity of the central line remains practically constant, whereas for the classical coexistence of phases the central line must be the continuity of the high-temperature component and its intensity must decrease down to zero in the low-temperature phase. However, the existence of this central line cannot be attributed to the possible disorientation of the sample, because in this case it would be observed in the low and high-temperature phases. Furthermore, the hypothesis of the line being related to another defect cannot be retained because similar behaviour would be observed in the two phases. Therefore, in order to account for the critical behaviour, the data have been fitted by the Landau free energy of first-order transitions

$$F = F_0 + \left[\alpha\left(T - T_0\right)/2\right]\eta^2 - (\gamma/4)\eta^4 + (\varepsilon/6)\eta^6$$

the minimization of which leads to

$$\frac{\langle\eta\rangle}{A_0} = \sqrt{0.5A_1 + \sqrt{A_2\left(T_1 - T\right)}} \text{ with } A_1 = \frac{\gamma}{\varepsilon} \qquad A_2 = \frac{\alpha}{\varepsilon} \qquad \text{and } T_1 - T_0 = \frac{A_1^2}{4A_2}$$

where $A_0$ is the coefficient related to the technique of measurement, $T_1$ is the existence limit of the low-temperature phase and $T_1 - T_0$ is the maximum temperature range where the phases can coexist. Figure 6(b) reports the adjustment of the splitting of the $3/2 \leftrightarrow 1/2$ transition for the $Cr^{3+}$ case and for the rotation around the $a$ axis $(\boldsymbol{H}, \boldsymbol{b}) = \pm 6^{\circ}$. The best agreement is obtained with the following parameters:

$A_0 = 332.0$ G $\qquad A_1 = 0.710 \pm 0.005 \qquad A_2 = 0.0239 \pm 0.0003\,^{\circ}\mathrm{C}^{-1}$

$T_1 = 208.40\,^{\circ}\mathrm{C} \qquad T_1 - T_0 = 5.28\,^{\circ}\mathrm{C} \pm 0.20\,^{\circ}\mathrm{C}.$

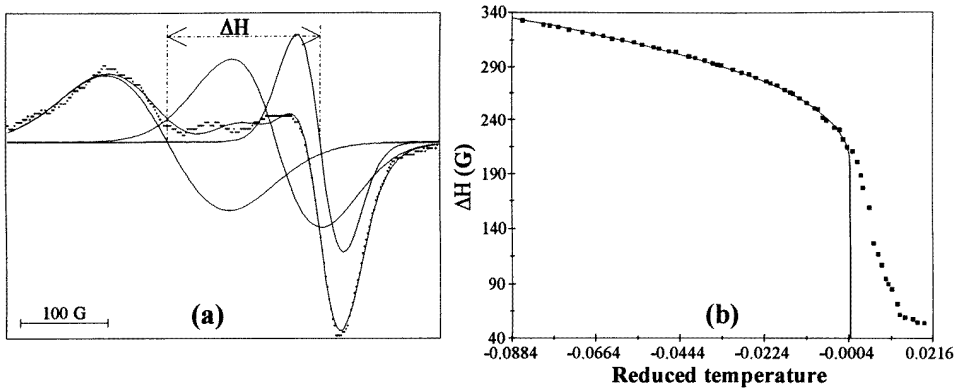


**Figure 6.** The $3/2 \leftrightarrow 1/2$ transition for the $Cr^{3+}$ probe: (a) reconstruction at $T - T_C = 2\,^{\circ}$C; (b) splitting versus the temperature for the rotation around the $a$ axis $(\boldsymbol{H}, \boldsymbol{b}) = \pm 6^{\circ}$. The coexistence of phases is characterized by the superposition of the three discrete lines. The splitting of the line is fitted by the Landau theory of first order $\Delta H = 332.0\sqrt{0.355 + \sqrt{0.0239\,(208.40 - T)}}$.

These parameters lead to the transition temperature $T_C = 207.10\,^{\circ}$C and to the order parameter jump $\langle \eta(T_C) \rangle / A_0 = 0.84$. Similar parameters have been obtained in squaric acid using high-resolution $^{13}$C NMR [10]. It should be noted that interpretation of the diffractometric results in the $KFeF_4$ isotype compound by Saint Grégoire *et al* [6] with the model of coexistence of phases proved to be successful.

## 5. Diffractometric measurements

In order to obtain complementary information, measurements of the intensity of the superstructure reflections have been performed. Near the transition, this intensity can exhibit a critical behaviour. Indeed, these superlattice reflections are characteristic of the low-temperature phase; therefore, the measure of their intensity versus the temperature leads to the order parameter $I(T) \propto \langle \eta^2(T) \rangle$, which includes the fluctuations.

We chose the superstructure reflection 310 and the temperature dependence was studied from room temperature up to $210\,^{\circ}$C. The value of the intensity corresponds to the $2\theta$ scanning of the Bragg reflection. The evolution of $I$ as a function of temperature is shown in figure 7. The data have been fitted with the critical law $I(T) \propto (201.22 - T)^{2\beta}$ (see figure 7(a)). The best agreement is obtained with

$$6.06 \times 10^{-3} \leqslant t \leqslant 0.205 \qquad 2\beta = 0.293 \pm 0.012.$$

This result is in agreement with our result from the previous section. Even when the $\beta$ critical exponent is determined outside the asymptotic critical region (i.e. $2\beta = 0.305 \pm 0.013$ for $7.55 \times 10^{-3} \leqslant t \leqslant 0.479$), it differs considerably from the one found in similar studies in $KFeF_4$ [6]. It is interesting to note that just above $T_C$, the intensity is non-zero, but it vanishes only $10\,^{\circ}$C or more above. Similar behaviour has been observed in the $KFeF_4$ isotype compound [6]. In addition, the divergence of the linewidth of the corresponding reflection has never been observed at the transition, but only $10\,^{\circ}$C above $T_C$. Furthermore, the splitting of a few reflections in the vicinity of $T_C$ is in agreement with the coexistence of phases. Therefore, as in the EPR results, the variation of $I(T)$ has been described by

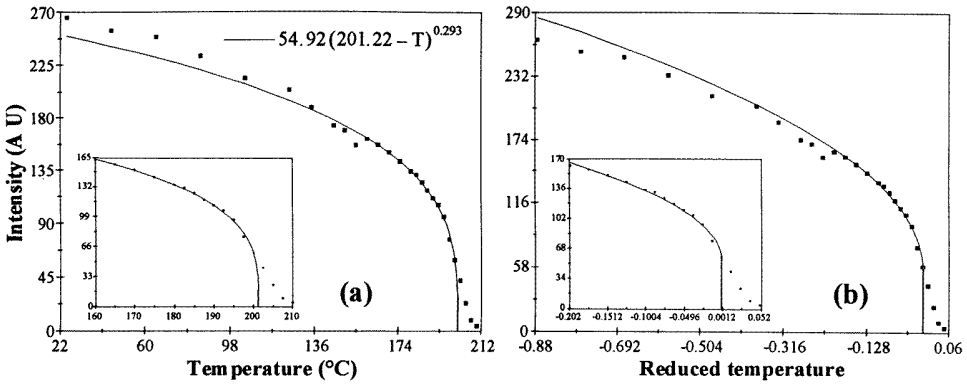


**Figure 7.** Intensity of the superstructure reflection 310 versus the temperature: (a) the $\beta$ critical exponent measured by fitting $I(T)$ with a critical law $I_0(201.22 - T)^{2\beta}$, $2\beta = 0.293 \pm 0.012$; (b) the intensity is fitted by the Landau theory of first-order $I = 127.2 \times (0.435 + \sqrt{0.0188(200 - T)})$.

the order parameter

$$\langle \eta^2 \rangle / A_0 = 0.5A_1 + \sqrt{A_2(T_1 - T)}.$$

The result of the fit is satisfactory and leads to

$$A_0 = 127.2 \qquad A_1 = 0.870 \pm 0.015 \qquad A_2 = 0.0188 \pm 0.0006\,^{\circ}\mathrm{C}^{-1}$$
$$T_1 = 200\,^{\circ}\mathrm{C} \qquad T_1 - T_0 = 10\,^{\circ}\mathrm{C} \pm 1\,^{\circ}\mathrm{C}.$$

these parameters can be converted into the transition temperature $T_C = 197.5\,^{\circ}\mathrm{C}$ and the order parameter jump $\sqrt{\langle \eta^2(T_C) \rangle / A_0} = 0.93$, respectively. The corresponding curve is presented in figure 7(b). In contrast to the EPR results, the maximum temperature range $(T_1 - T_0)$ where the coexistence of phases can be observed is very important.

## 6. Conclusion

We have used the EPR and x-ray techniques for a single crystal to study the critical behaviour of the $KGaF_4$ layered compound. The main results can be summarized as follows.

Preliminary dilatometric study allowed us to determine the main mechanism of the phase transition. Then in the EPR section, by the reconstruction of many spectra in several orientations of magnetic field and by the analysis of the shape of the lines in the critical region, the hypothesis of the continuous or quasi-continuous approach has been excluded. Indeed, a second-order transition is not in agreement with the angle ($\phi_c = 8.04^{\circ} \pm 0.15^{\circ}$) of the rotation of the octahedra around the $c$ axis, which remains high at the transition ($\phi_c \approx 5^{\circ}$ at $T_C - T \approx 0.5^{\circ}$). Nevertheless, the interpretation of the phase transition in this approach ($\beta = 0.140$) allows us to conclude that this latter is essentially 2D in character. As in the $KFeF_4$ isotype compound, this result is consistent with the fact that the coupling between adjacent layers is cancelled due to symmetry arguments, leading to a much weaker interlayer coupling.

From our EPR studies, it becomes evident that only the discontinuous approach allows us to account for the critical behaviour. Diffractometric measurements are in agreement

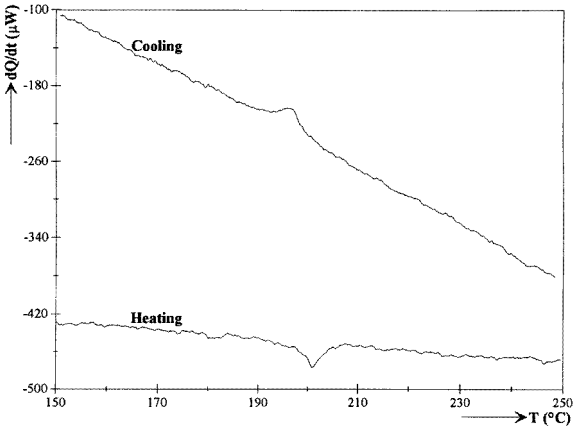


**Figure 8.** The DSC single-crystal signal for the heating and cooling loop. The sample weight is 3.44 mg and the scan rate is 5 °C $min^{-1}$.

with this result, but the temperature range where the coexistence of phases can be observed is more important. This could be due to the short-range local probing.

DSC measurements on a single crystal have been performed and the results for the sample weight 3.44 mg are as follows: the discontinuity of the specific heat is 0.5 J $g^{-1}$ during heating ($T_C = 201.2\,^{\circ}$C) and $-0.4$ J $g^{-1}$ during cooling ($T_C = 196.6\,^{\circ}$C; see figure 8). The corresponding hysteresis is $2 \leqslant \Delta T \leqslant 4.6\,^{\circ}$C. With these results, the first-order character is clear, but the discontinuity is weak. This is consistent with the fact that the coexistence of two ordered phases is not clearly proved. Therefore, we can suppose the coexistence of partially disordered phases, or following Bianchi and Saint Grégoire [4, 11], the presence of an intermediate modulated phase between phase II and phase III. However, satellite reflections characteristic of the incommensurable phase have never been observed. The possible solutions may be obtained with studies of the dynamic critical behaviour.

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## References

[1] Courbion G, Randrianohavy J V and Rousseau J 1989 *J. Solid State Chem.* **81** 285–92
[2] Randrianohavy J V 1991 *Thesis* Le Mans
[3] Fouejio D and Rousseau J J 1996 *J. Phys.: Condens. Matter* **8** 2663–72
[4] Bianchi U, Kleemann W and Saint Grégoire P 1991 *Phase Transitions* **36** 155–64
[5] Sciau Ph and Grebille D 1989 *Phys. Rev.* B **39** 11 982–92
[6] Saint Grégoire P, Perez A, Almairec R and Lopez M 1985 *Phys. Status Solidi* a **87** K1
[7] Nouet J, Jacoboni C, Ferey G, Gerard J Y and De Pape R 1971 *J. Cryst. Growth* **8** 94
[8] Keller H and Savic I M 1983 *Phys. Rev.* B **28** 2638–52
[9] Heger G and Geller R 1972 *Phys. Status Solidi* b **53** 227
[10] Mehring M and Becker J D 1981 *Phys. Rev. Lett.* **47** 366–70
[11] Saint Grégoire P and Perez A 1983 *Z. Kristallogr.* **163** 135–8