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Mössbauer studies of the structural phase transitions in RbFeF_4

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Abstract. RbFeF_4 exhibits two structural phase transitions (SPT), namely a first-order transition at $T_{c_1} = 381$ K and a second-order transition at $T_{c_2} = 417$ K. A detailed ^{57}Fe Mössbauer investigation of these SPT is presented. At T_{c_1} pronounced discontinuities in the quadrupole splitting and the recoil-free fraction are observed, whereas at T_{c_2} both quantities vary continuously with temperature. Both SPT are also seen in the area ratio of the single crystal quadrupole lines which reflects the tilting of the FeF_6 octahedra with respect to the c -axis. However, no noticeable indication of the SPT is found in the center shift.

I. Introduction

During the past few years, the layered antiferromagnets of the form XFeF_4 ($\text{X} = \text{Rb}, \text{K}, \text{Cs}$) have been investigated extensively because of their interesting magnetic properties [1–5]. However, until lately, not much attention has been paid to the structural properties of these compounds. Recently, Hidaka et al. [6] have found two new structural phase transitions (SPT) in RbFeF_4 and CsFeF_4 by means of X-ray diffraction, specific heat, optical, and dielectric measurements. RbFeF_4 , which is the subject of this study, shows a first-order transition at $T_{c_1} = 378$ K and a second-order transition at $T_{c_2} = 418$ K. CsFeF_4 has similar SPT at somewhat higher transition temperatures. These SPT have been interpreted by a simple model [6] based on the rotation of FeF_6 octahedra around the crystallographic axes (Fig. 1). Since the FeF_6 octahedra are arranged in weakly coupled layers, the phase transitions are thought to be quasi two-dimensional in nature.

In this paper, we report a detailed ^{57}Fe Mössbauer investigation of the SPT in RbFeF_4 . In Section II we briefly review the structural properties of RbFeF_4 together with the results of the Oxford group [6]. The experimental details and the results are presented in Section III, and the conclusions follow in Section IV.

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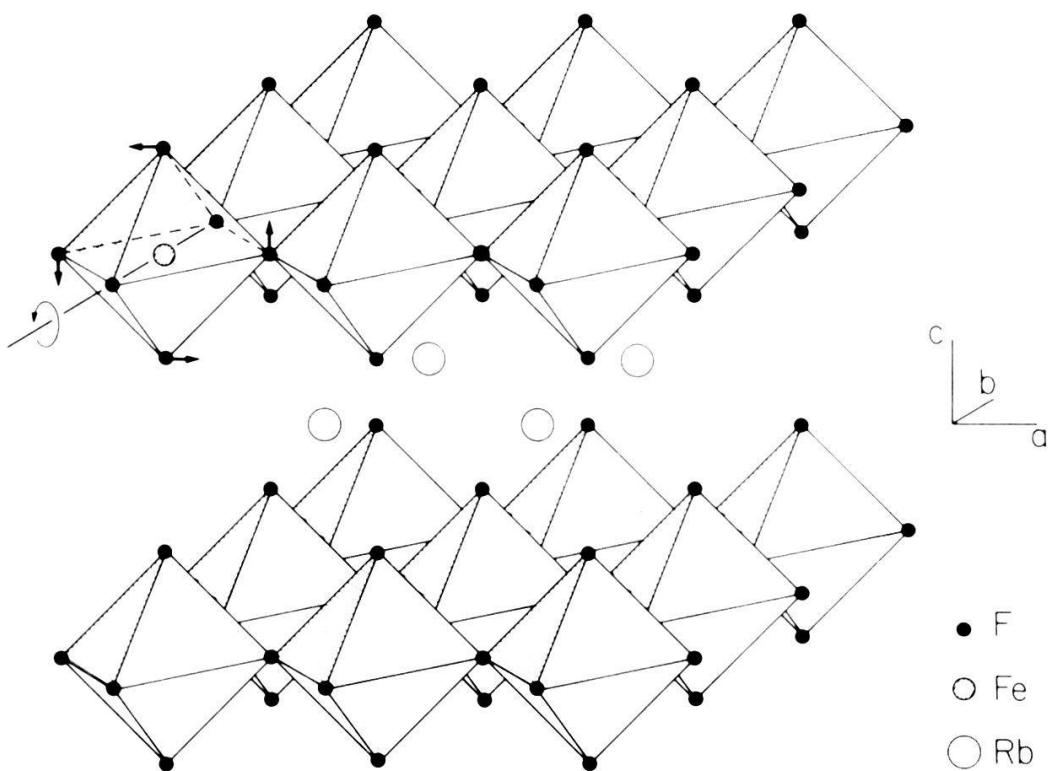


Figure 1
Idealized crystal structure of RbFeF_4 . The FeF_6 octahedra are shown without distortion or tilting. The arrows indicate the rotations of the octahedra in phase II.

II. Crystal structure and phases

At room temperature (RT) RbFeF_4 is known to be orthorhombic with lattice constants $a = 7.615 \text{ \AA}$, $b = 7.620 \text{ \AA}$, and $c = 6.245 \text{ \AA}$ [7–9]. The RT structure consists of slightly tilted and tetragonally distorted FeF_6 octahedra with layers of Rb^+ ions in between (Fig. 1).

The three structural phases above T_N , here denoted as phase I to III, have been characterized by the Oxford group [6]. Their results are summarized in Table I. In the tetragonal high-temperature phase I the FeF_6 octahedra are not tilted, and one has the TiAlF_4 -type structure. In the lower-symmetry orthorhombic phases II and III the FeF_6 octahedra are tilted with respect to the c -axis. The

Table I
Structural properties of RbFeF_4 [after Hidaka et al. (Ref. 6)]. Z is the number of molecules per unit cell.

Transition temperature	Phase	Space group	Z	Tilting scheme of Glazer ^{a)}
$T_{c_2} = 418(417) \text{ K}^b)$ second-order	I	$\text{P}4/\text{mmm} (D_{4h}^1)$	1	$a^0 a^0 c^0$
	II	$\text{Pmmn} (D_{2h}^5)$	2	$a^0 b^+ c^0$
$T_{c_1} = 378(381) \text{ K}^b)$ first-order	III	$\text{P}2_1 2_1 2 (D_2^3)$	4	$a^+ b^+ c^0, a^+ b^+ c^+$

^{a)} Reference 10.

^{b)} Values in parentheses are from this work.

tilting of the octahedra may be described in each phase by adopting the octahedral tilting representation of Glazer [10] (see Table I). As an example, in this notation $a^0b^+c^0$ means a positive tilt (sign arbitrarily defined) of magnitude b about the pseudotetragonal axis [010], whereas $a^0a^0c^0$ corresponds to the un-tilted structure. Starting from the tetragonal phase I the unit cell is first doubled along [100] in phase II ($a^0b^+c^0$) and then further doubled along [010] in the RT phase III ($a^+b^+c^0$ or $a^+b^+c^+$) as shown in Table I. However, the c -axis is not doubled in either case, probably suggesting that the tilting of the FeF_6 octahedra and thus the SPT are quasi two-dimensional in character.

According to Hidaka et al. [6], the SPT are associated with the condensation of soft-phonon modes at the X zone-boundary points of the Brillouin zone of the highest-symmetry phase I. The corresponding soft-phonon modes at T_{c_2} and T_{c_1} have wavevectors $q = (\frac{1}{2}, 0, 0)$ and $q = (0, \frac{1}{2}, 0)$, respectively. The space group of phase II (D_{2h}^5) is a subgroup of the high-symmetry parent phase I (D_{4h}^1), a necessary condition for a second-order phase transition in the concept of the Landau theory [11]. Moreover, the transition at T_{c_1} is not truly first-order in character since the low-temperature phase III (D_2^3) is still a subgroup of the high-temperature phase II (D_{2h}^5). Such a transition is usually denoted "weak" first-order [11].

III. Experimental details and results

Single-crystal platelets of RbFeF_4 were prepared by the flux method, in crucibles of platinum with closely-fitting lids [12]. The flux was PbCl_2 , and NH_4HF_2 was included to convert any oxide materials present into the corresponding fluorides. To reduce oxidation and hydrolysis, the rate of cooling was a relatively fast 5°C per hour. Thin platelets up to $15 \times 15 \times 0.3 \text{ mm}^3$ were obtained. These were colourless to orange, indicating the presence of little, if any, Fe^{2+} in the lattice.

All Mössbauer measurements were performed on single-crystal samples with the direction of the γ -rays perpendicular to the FeF_6 layers. Crystals with typical dimension of $4 \times 4 \times 0.3 \text{ mm}^3$ were mounted stress-free between pure aluminium foils in copper sample holders. Measurements in the temperature range 300–480 K were taken in a high-vacuum furnace. The sample temperature was controlled with a chromel-alumel thermocouple and constantly recorded on a chart recorder. In this way, a relative long-term temperature stability of better than ± 0.1 K was obtained. The absolute temperature accuracy was estimated to be ± 1.5 K. The measurements were performed with a conventional constant acceleration spectrometer with a 25 mCi $^{57}\text{CoRh}$ source.

Typical Mössbauer spectra taken in each phase (Table I) are shown in Fig. 2. The spectra consist of a pure asymmetric quadrupole doublet with experimental linewidths (full width at half maximum) of 0.24 and 0.23 mm/s in phase I and III, respectively. It is known from the low-temperature magnetic hyperfine spectra [2, 3, 5] that in phase III the electric field gradient (EFG) tensor is axially symmetric ($\eta = 0$). Furthermore, the angle θ_γ between the principal axis of the EFG tensor V_{zz} and the c -axis was found to be $16 \pm 1^\circ$, which is consistent with the tilting angle $\phi \approx 18^\circ$ of the FeF_6 octahedra at room temperature [2, 3, 5]. In this work, we assume that θ_γ is a suitable quantity (order parameter) to describe

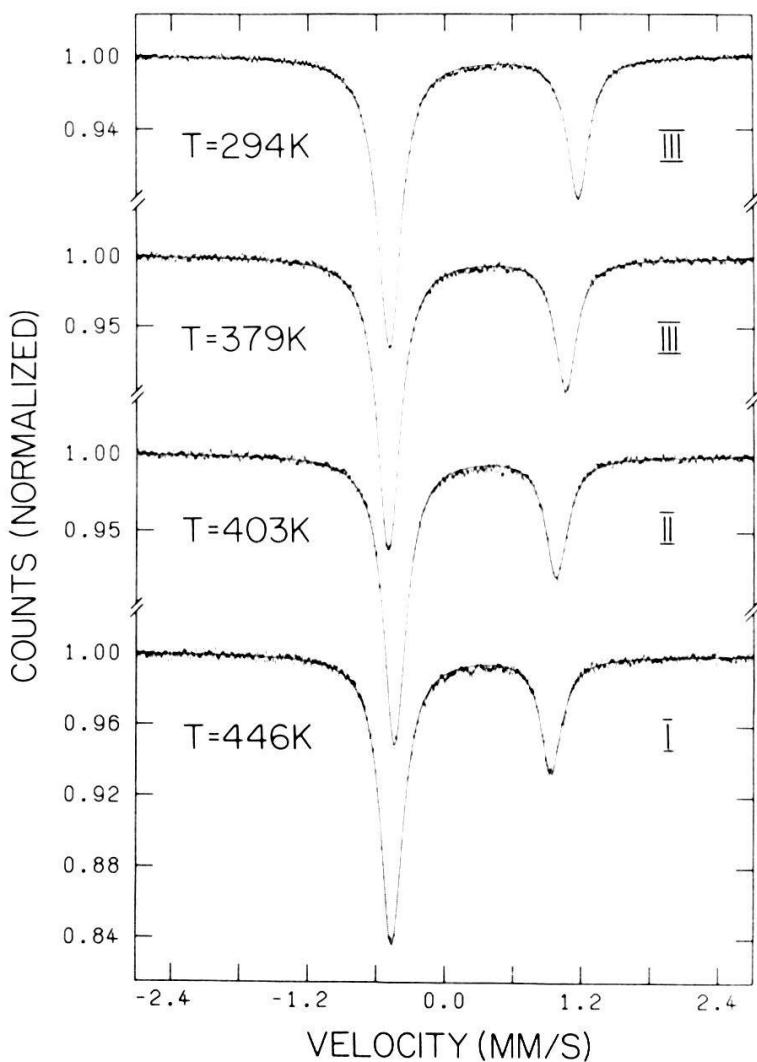


Figure 2
Mössbauer spectra of single-crystal RbFeF_4 taken at various temperatures in each phase (see Table I).

the tilting of the octahedra. The angle θ_γ is directly related to the intensity ratio R of the two quadrupole lines. Neglecting polarization effects [2], for thin crystals R is approximately given by

$$R = \frac{I(\Delta m = 0)}{I(\Delta m = \pm 1)} = \frac{2/3 + \sin^2 \theta_\gamma}{1 + \cos^2 \theta_\gamma}. \quad (1)$$

In the high-temperature phase I, R (corrected for the finite sample thickness) was found to be roughly $\frac{1}{3}$, indicating that $\theta_\gamma = 0$ (untilted structure). It is obvious from Fig. 2 that V_{zz} is negative since the more intense lines ($\Delta m = \pm 1$) are at lower velocities.

The temperature dependence of the quadrupole splitting Δ is shown in Fig. 3a, where both SPT are evident. At the first-order transition, $T_{c_1} = 381$ K, an abrupt jump in Δ of roughly 0.1 mm/s is observed. Near $T_{c_2} = 417$ K, on the other hand, Δ varies continuously, as expected for a second-order transition, and Δ remains constant in the highest symmetry phase I. A similar, but less pronounced discontinuity in Δ near 380 K has previously been observed in powder samples by

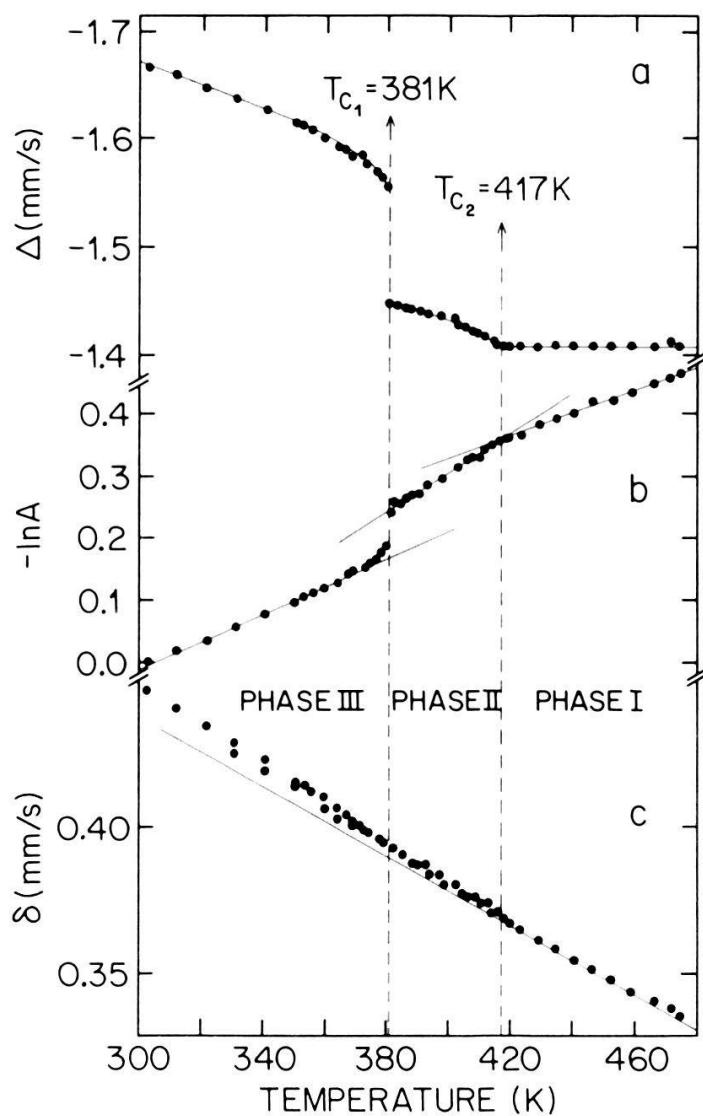


Figure 3

Temperature dependence of various Mössbauer parameters in phase I, II, and III. Data points are from different runs with increasing and decreasing temperature. For clarity, not all measured points are shown. (a) Quadrupole splitting Δ . The solid line is intended to guide the eye. (b) Relative effective mean-square displacement ($-\ln A$ in arbitrary units). The straight lines represent least-squares fits through the data points. (c) Center shift δ . The straight line corresponds to the slope of δ in phase I and is intended to guide the eye.

Teillet et al. [13]. However, no indication of a second-order transition is seen in their data. The temperature dependence of Δ is consistent with the fact that the crystal symmetry is lowered by decreasing the temperature from phase I to II and from phase II to III (Fig. 3a). The values for Δ are unusually large for high-spin Fe^{3+} [1, 14], whereas the values for the center shift δ are typical for this electronic configuration (Fig. 3c). Recently, Teillet et al. [14] have used a polarizable point charge model to calculate the EFG in $RbFeF_4$ at room temperature. According to these authors, the large EFG is most likely due to the non-bridging fluorine ions in the FeF_6 layers. No attempt was made in this work to interpret the measured temperature dependence of Δ with this model.

The total area A of the absorption lines in thin absorbers is proportional to

the recoilless fraction f . In the harmonic approximation we may write [15–17]

$$A \propto f = \exp(-k^2 \langle x^2 \rangle), \quad (2)$$

or

$$-\ln A = c_0 + k^2 \langle x^2 \rangle, \quad (3)$$

where $\langle x^2 \rangle$ is the mean-square displacement (msd) of the ^{57}Fe nucleus along the wave vector \vec{k} of the γ -rays, and c_0 is a numerical constant which must be determined experimentally. In the classical high-temperature limit ($T > \theta_D/2$) the Debye model yields

$$\langle x^2 \rangle = 3\hbar^2 T / (m_* k_B \theta_D^2). \quad (4)$$

Here θ_D is the Debye temperature, and m_* is the effective mass of ^{57}Fe .

Figure 3b shows the temperature dependence of $-\ln A$ (relative msd in arbitrary units). At the first-order transition a distinct discontinuity in $-\ln A$ is observed. This anomaly may be understood qualitatively in terms of a simple model. In the low-temperature phase III the Fe^{3+} ion is in a potential A , and the corresponding effective msd is given by $\langle x_*^2 \rangle_A = c_{\text{III}} + a_{\text{III}} T$ (high-temperature approximation). However, at T_{c_1} the shape of the potential changes abruptly due to the sudden reorientation of the FeF_6 octahedra. As a result, in phase II the thermal motion of the iron atom is determined by a different potential B with $\langle x_*^2 \rangle_B = c_{\text{II}} + a_{\text{II}} T$. Using equation (3), the absolute change of $\langle x_*^2 \rangle$ at T_{c_1} is:

$$\Delta \langle x_*^2 \rangle = \Delta c + \Delta a T_{c_1}, \quad (5)$$

where $\Delta c = c_{\text{II}} - c_{\text{III}}$ and $\Delta a = a_{\text{II}} - a_{\text{III}}$ are determined by the straight lines in Fig. 3b. We find $\Delta \langle x_*^2 \rangle \approx 1.6 \times 10^{-3} \text{ \AA}^2$. For harmonic potentials, Δc in equation (5) is zero [15, 16]. In our case Δc is negative, indicating deviations from a harmonic potential (low-temperature anharmonicity) [16, 17], at least in the lower-symmetry phase III. Note that just below T_{c_1} a slight deviation of the effective msd from a straight line is observed (Fig. 3b). This is likely to be due to anharmonicity effects [16] which probably play an important role in triggering the first-order transition. However, no such effect is seen in phase II above T_{c_1} . One can clearly distinguish the three phases by their different slopes in $-\ln A$ as shown in Fig. 3b. The corresponding Debye temperatures θ_D as obtained from equation (4) are:

$$\theta_D^{\text{I}} = 276 \pm 5 \text{ K}, \quad \theta_D^{\text{II}} = 210 \pm 3 \text{ K}, \quad \theta_D^{\text{III}} = 246 \pm 3 \text{ K},$$

where it is assumed that m_* is the mass of ^{57}Fe . Note that these values for θ_D are significantly lower than $\theta_D = 495 \pm 50 \text{ K}$, deduced from thermal-shift measurements in phase III [5]. For a detailed discussion of this problem we refer to Ref. 17.

No noticeable indication of the SPT was found in the center shift δ (Fig. 3c), especially at the first-order transition where an anomalous behavior is expected. There is only a slight continuous change in δ going from phase I to III. This may be understood as follows. The center shift δ is the sum of two different contributions [5, 17]:

$$\delta = \delta_{\text{IS}} - \langle v^2 \rangle / 2c. \quad (6)$$

The isomer shift δ_{IS} is usually larger than the second term and is in general only

weakly temperature dependent. The second-order Doppler shift $-\langle v^2 \rangle/2c$ is a relativistic effect which is due to the thermal motion of the ^{57}Fe nucleus in the lattice. It is proportional to the mean-square velocity (msv) $\langle v^2 \rangle$ of the ^{57}Fe nucleus. A calculation of $\langle v^2 \rangle$ involves a summation over the entire vibration spectrum of the lattice. In a general harmonic model [15, 17], this summation is weighted by factors ω_j , where ω_j is the angular frequency of the j th normal mode. For $\langle x^2 \rangle$, on the other hand, the corresponding weighting factor in the summation is ω_j^{-1} [15, 17]. Hence $\langle x^2 \rangle$ is more sensitive to low frequency modes than is $\langle v^2 \rangle$. The SPT are associated with the condensation of soft phonon modes (cf. Section II) whose frequencies $\omega_s(q)$ tend to go to zero at T_c [11]. Therefore one would expect a stronger effect in $-\ln A$ (msd) than in δ (msv), in agreement with our observations. Notice that at the magnetic transition, $T_N = 136.6$ K, a magnetically induced anomaly in δ is observed [5].

The temperature dependence of the experimental line area ratio $R = A_R/A_L$ (uncorrected for self-absorption) is shown in Fig. 4. This quantity clearly reflects the increasing tilting of the FeF_6 octahedra with respect to the c -axis [cf. equation (1)] as the temperature is lowered from phase I to phase III. In the high-temperature tetragonal phase (untilted structure) A_R/A_L remains constant and is roughly $\frac{1}{3}(\theta_\gamma \approx 0)$, taking self-absorption corrections into account. At the first-order transition, A_R/A_L varies more rapidly than at T_{c_2} , where a smooth change in A_R/A_L is observed that is characteristic for a second-order transition. However, no discontinuity in A_R/A_L is detectable at T_{c_1} .

It is known that at a second-order phase transition (T_c), the order parameter $\Phi(T)$ vanishes continuously as

$$\Phi(T) \propto (1 - T/T_c)^\beta, \quad T \leq T_c, \quad (7)$$

where β is the critical exponent of the order parameter. Here Φ is proportional to the tilting angle ϕ of the FeF_6 octahedra in phase II. Assuming that $\phi \approx \theta_\gamma$, where θ_γ is the angle between the principal axis of the EFG tensor V_{zz} and the c -axis,

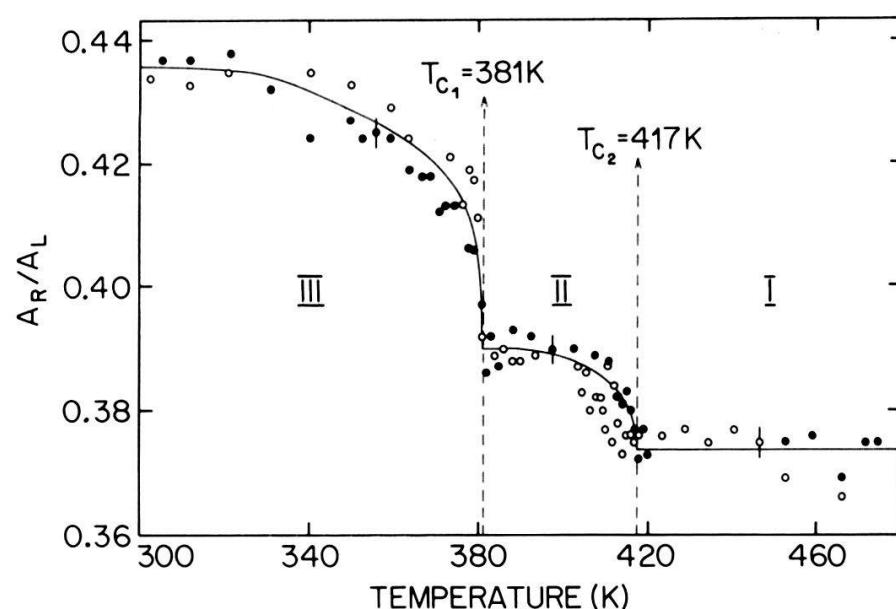


Figure 4
Temperature dependence of the experimental area ratio A_R/A_L , uncorrected for self-absorption (● increasing temperature, ○ decreasing temperature). The solid line is intended to guide the eye.

we may use equation (7) to estimate β . A best fit of the experimental data to this power law in the reduced temperature range, $5.5 \times 10^{-4} < 1 - T/T_{c_2} < 3.5 \times 10^{-2}$, yields: $T_{c_2} = 417.15 \pm 0.20$ K and $\beta = 0.36 \pm 0.08$. The fit is rather poor due to the large experimental errors of θ_y (see Fig. 4), and thus this value of β should only be considered as a rough estimate. The present value of $\beta = 0.36 \pm 0.08$ seems to exhibit a deviation from mean-field behavior ($\beta = 0.5$) indicating that fluctuations of the order parameter are important near T_{c_2} . For comparison, a value of $\beta \approx \frac{1}{3}$ is typical for a three-dimensional system with short-range interactions, in contrast to a two-dimensional system where a value close to $\beta = \frac{1}{8}$ (2D Ising model) is expected [5].

No hysteresis effects were observed at either transition in increasing and decreasing the temperature (Fig. 3), except for a slight systematic deviation in the area ratio A_R/A_L (Fig. 4). Hysteresis effects are usually seen at first-order transitions. The transition temperatures agree with those obtained by the Oxford group [6] as listed in Table I. Finally, at both SPT a broadening of the quadrupole lines is observed that is most likely due to sample and temperature inhomogeneities.

IV. Conclusions

We have used the Mössbauer technique to investigate the structural phase transitions in RbFeF_4 . Our findings are essentially in accordance with the previous results of Hidaka et al. [6]. We conclude that the transitions at $T_{c_1} = 381$ K and $T_{c_2} = 417$ K are “weak” first-order and second-order in character, respectively. Our results are also consistent with the simple model proposed by the Oxford group [6]. According to this model, the SPT may be interpreted in terms of simple rotations of FeF_6 octahedra around the crystallographic a and b axes. In particular, at T_{c_1} a distinct jump in the quadrupole splitting and a discontinuity in the effective mean-square displacement are observed that are most likely induced by a sudden reorientation and slight deformation of the FeF_6 octahedra. At T_{c_2} , on the other hand, all measured quantities vary continuously with temperature as expected for a second-order phase transition.

The present estimate of the critical exponent $\beta = 0.36 \pm 0.08$ seems to indicate a deviation from “classical” Landau behavior. The accuracy of β , however, is insufficient at present to draw any definite conclusions about the nature of the second-order transition. More experimental work is still required to get a better understanding of these structural phase transitions.

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REFERENCES

- [1] See, e.g., M. EIBSCHÜTZ, G. R. DAVIDSON, and H. J. GUGGENHEIM, Phys. Rev. B9, 3885 (1974), and references therein.
- [2] J. D. RUSH, A. SIMOPOULOS, M. F. THOMAS, and B. M. WANKLYN, Solid State Commun. 18, 1039 (1976).

- [3] I. M. SAVIĆ, H. KELLER, W. KÜNDIG, and P. F. MEIER, Phys. Lett. 83A, 471 (1981).
- [4] I. M. SAVIĆ and H. KELLER, Helv. Phys. Acta 54, 234 (1981); 54, 603 (1981).
- [5] H. KELLER and I. M. SAVIĆ, Phys. Rev. B28, 2638 (1983), and references therein.
- [6] M. HIDAKA, I. G. WOOD, B. M. WANKLYN, and B. J. GARRARD, J. Phys. C12, 1799 (1979).
- [7] D. BABEL, Z. Naturforsch. 23a, 1417 (1968).
- [8] A. TRESSAUD, J. GALY, and J. PORTIER, Bull. Soc. Fr. Mineral. Cristallogr. 92, 335 (1969).
- [9] D. BABEL, F. WALL, and G. HEGER, Z. Naturforsch. 29b, 139 (1974).
- [10] A. M. GLAZER, Acta Crystallogr. B28, 3384 (1972); A31, 756 (1975).
- [11] See, e.g., K. A. MÜLLER, in *Structural Phase Transitions I*, edited by K. A. MÜLLER and H. THOMAS (Springer-Verlag, New York, 1981), p. 1.
- [12] B. M. WANKLYN, F. R. WONDRE, A. MAQSOOD, K. YANAGISAWA, and W. DAVISON, J. Mat. Sci. 14, 1447 (1979).
- [13] J. TEILLET, G. FEREY, M. LEBLANC, and F. VARRET, Solid State Commun. 27, 1083 (1978).
- [14] J. TEILLET, Y. CALAGE, and F. VARRET, J. Phys. Chem. Solids 43, 863 (1982).
- [15] R. M. HOUSLEY and F. HESS, Phys. Rev. 146, 517 (1966).
- [16] J. G. DASH, D. P. JOHNSON, and W. M. VISSCHER, Phys. Rev. 168, 1087 (1968).
- [17] L. D. LAFLEUR and C. GOODMAN, Phys. Rev. B4, 2915 (1971).