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## A Mössbauer study of $\text{Rb}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$

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**Abstract.** Mössbauer absorption spectra have been recorded for powder and single-crystal samples of the antiferromagnetic compound  $\text{Rb}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  over the temperature range 1.4–293 K and also at 4.2 K in applied magnetic fields up to 10 T. Electrostatic hyperfine interaction parameters have been deduced from the paramagnetic spectra. At 4.2 K an external field of 1.74 T applied along the (magnetic easy)  $a$  axis reoriented the Fe spins to the  $c$  axis. The spin-reorientation phase transition was found to be very sharp and with a small hysteresis. Comparisons are made with recent studies of  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  and  $\text{K}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$ .

### 1. Introduction

The compounds  $\text{A}_2\text{FeX}_5\cdot\text{H}_2\text{O}$  ( $\text{A}$  = alkali metal or ammonium ion and  $\text{X}$  = halogen) are antiferromagnetic with Néel temperatures in the 5–25 K range. Their crystallographic and magnetic properties have been reviewed by Carlin and Palacio [1]. Among this family  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  had been reported to have some unusual properties (for example [2]): two heat capacity cusps in the region of the Néel temperature  $T_N \approx 7$  K and magnetic susceptibility data not characteristic of a pure antiferromagnet. In Mössbauer experiments on this compound [3, 4] we were able to show, for example, that the extra heat capacity cusp was not due to a temperature-induced spin reorientation, as had been suggested earlier. Neither was there a large canting of the Fe spins, supposedly responsible for the susceptibility results. Our experiments also showed the existence of more than one spectral component in the antiferromagnetic region and a continuous (second-order) field-driven spin-reorientation phase transition.

In order to establish whether these and other properties are indeed unique to  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  we have made Mössbauer measurements on  $\text{K}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  [5] and  $\text{Rb}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$ , reported here. Thus this is the last of the present series of Mössbauer studies on these three compounds. Because of the similarity in procedures to those in [5] the account here is shorter; fuller details may be found, if required, in the earlier articles. As before, the emphasis is on the results obtained with single-crystal absorbers.

### 2. Experimental details

Single crystals of  $\text{Rb}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  were grown from hydrochloric acid solution following the method of O'Connor *et al* [6]. The crystal growth habits were similar to those reported [3, 5] for  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  and  $\text{K}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$ . The assignment of crystal axes was verified by oscillation x-ray photography. Single-crystal Mössbauer absorbers typically 25 mm<sup>2</sup> in area were prepared by setting crystals in low-temperature epoxy, abrading to produce platelets

in the appropriate crystal planes, thinning by finer abrasion (5  $\mu\text{m}$  emery) to the optimum thickness for Mössbauer absorption experiments and finally sealing with more epoxy. The powder sample of thickness approximately  $40 \text{ mg cm}^{-2}$  was prepared from ground crystals mixed with a similar mass of boron nitride.

Mössbauer spectra were taken with four spectrometers: a room-temperature spectrometer, a continuous helium-flow cryostat for temperatures above 4.2 K, a liquid-helium spectrometer with pumping facility for temperatures in the 1.3–4.2 K range and a 10 T superconducting magnet cryostat. In the flow cryostat measurements, the sample temperature was monitored using a carbon-glass resistor located in the sample mount. The uncertainty of the temperature measurement was approximately  $\pm 0.1 \text{ K}$ . The Mössbauer  $\gamma$ -ray sources were  $^{57}\text{Co/Rh}$  and the constant acceleration spectrometer drives were operated in double-ramp (flat background) mode.

### 3. Zero-field spectra

#### 3.1. Powder spectra

These showed a well-resolved doublet above  $T_N$  and a single sextet component below  $T_N$ . Apart from some expected broadening at temperatures close to  $T_N$ , the linewidth was typically  $0.27 \text{ mm s}^{-1}$  throughout this work. Fitted spectral parameters at selected temperatures are given in table 1. The quadrupole splitting is almost temperature independent within experimental error. Its magnitude is somewhat larger than the one value ( $0.31 \text{ mm s}^{-1}$  at room temperature) reported by Partiti *et al* [7]. The temperature dependence of the magnetic hyperfine field is shown in figure 1. The collapse to zero is consistent with the ordering temperature of  $T_N = 10.00 \pm 0.02 \text{ K}$  reported in the heat capacity measurements of Puértolas *et al* [8].

**Table 1.** Mössbauer parameters from powder spectra at selected temperatures: centre shift  $\delta$  relative to iron foil at room temperature, magnetic hyperfine field  $B_{\text{hf}}$ , quadrupole shift  $\epsilon$  and quadrupole splitting  $\Delta E_Q$ .

$T$ (K)	$\delta$ ( $\text{mm s}^{-1}$ )	$B_{\text{hf}}$ (T)	$2\epsilon$ ( $\text{mm s}^{-1}$ )	$\Delta E_Q$ ( $\text{mm s}^{-1}$ )
293	0.42	—	—	0.36
100	0.54	—	—	0.37
20	0.55	—	—	0.37
8	0.55	37.4	-0.05	
4.2	0.54	47.6	-0.06	
1.4	0.54	49.8	-0.06	

#### 3.2. Single-crystal spectra

Spectra were taken at various temperatures with *ab*-, *bc*- and *ac*-plane absorbers. Spectra taken at 4.2 K are shown in figure 2. The absence of 2, 5 line intensity for the *bc*-plane absorber and the approximately 3:4:1 intensity ratios for the other two absorbers verify that the Fe spins are aligned along the *a* axis, consistent with this generally being the magnetic easy axis for this family of compounds and with, in particular, the susceptibility measurements of Puértolas *et al* [8] for  $\text{Rb}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ .

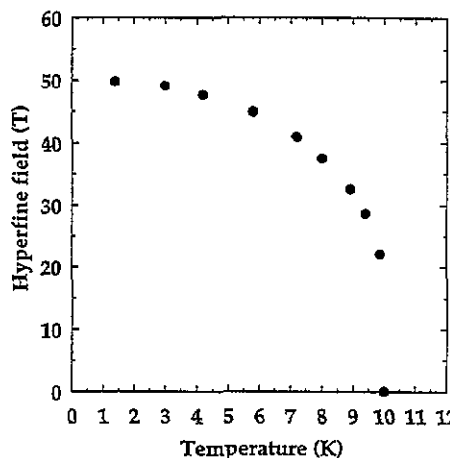


Figure 1. Temperature dependence of the magnetic hyperfine field.

Spectra in the paramagnetic region were taken to determine parameters of the electrostatic interaction using the same procedure as described before [3, 5]. Some of these are shown in figure 3. A complication in the present case was the appearance of an apparent contaminant component, found to be well fitted by a weaker doublet as shown in the lower spectra in figure 3. A similar effect had been noticed in the earlier  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  experiments but was weaker there, and only in some absorbers. Since the effect was not apparent in the case of the powder samples, presumably it is due to some other material produced in the abrasion process. The contaminant doublet disappears between 30 K and 20 K. The most likely explanation of this is that the contaminant material orders between these two temperatures. To check this we used the *ac*-absorber at 12 K (just above  $T_N$  for the title compound) with a velocity range higher than that shown in figure 3, and observed a sextet which, because of its broad lines, was only just discernible. Its absorption area was nevertheless approximately 20% of that of the central doublet and thus comparable with that of the contaminant doublet at 30 K, where no such sextet was discernible. We have not identified the contaminant material. The combination of  $B_{\text{hf}} \approx 44$  T at 12 K,  $\Delta E_Q \approx 0.75$  mm s<sup>-1</sup> and an ordering temperature between 20 K and 30 K rules out, for example, some common iron-chloride compounds. However, some confidence that we have correctly allowed for it comes from the good match between the parameters deduced for the title compound at 20 K and 30 K.

As in the previous experiments on  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  and  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ , self-consistent results followed from the starting hypothesis that the crystal *b* axis is one of the axes of the electric-field-gradient principal axes system (EFG PAS). We found  $V_{zz}$  to be negative and values of the asymmetry parameter  $\eta$  and  $\theta_a$  (the angle between the EFG *z* axis and the crystal *a* axis) as given in table 2. We conclude that  $\theta_a \approx 50^\circ$  and therefore, as in the other two cases, that the EFG *z* axis is not quite along the Fe-O bond line which is at  $38^\circ$  to the *a* axis in  $\text{Rb}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ . The value of  $\eta$  is smaller than those of the other two compounds, both of which have  $\eta \approx 0.6$  at low temperature. The latter similarity may be fortuitous because, as noted by Partiti *et al* [7], the EFG is sensitive to the positions of the water H ions. Bearing in mind that the random (fitting) error in  $\eta$  is approximately 0.05, we may conclude that  $\eta$  has a small but definite temperature dependence. This reinforces the suggestion of similar behaviour in the  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  case and the remark there [5] that the decrease of  $\eta$  with temperature for the  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  compound may not be entirely due to the motion of the  $\text{NH}_4$  ions.

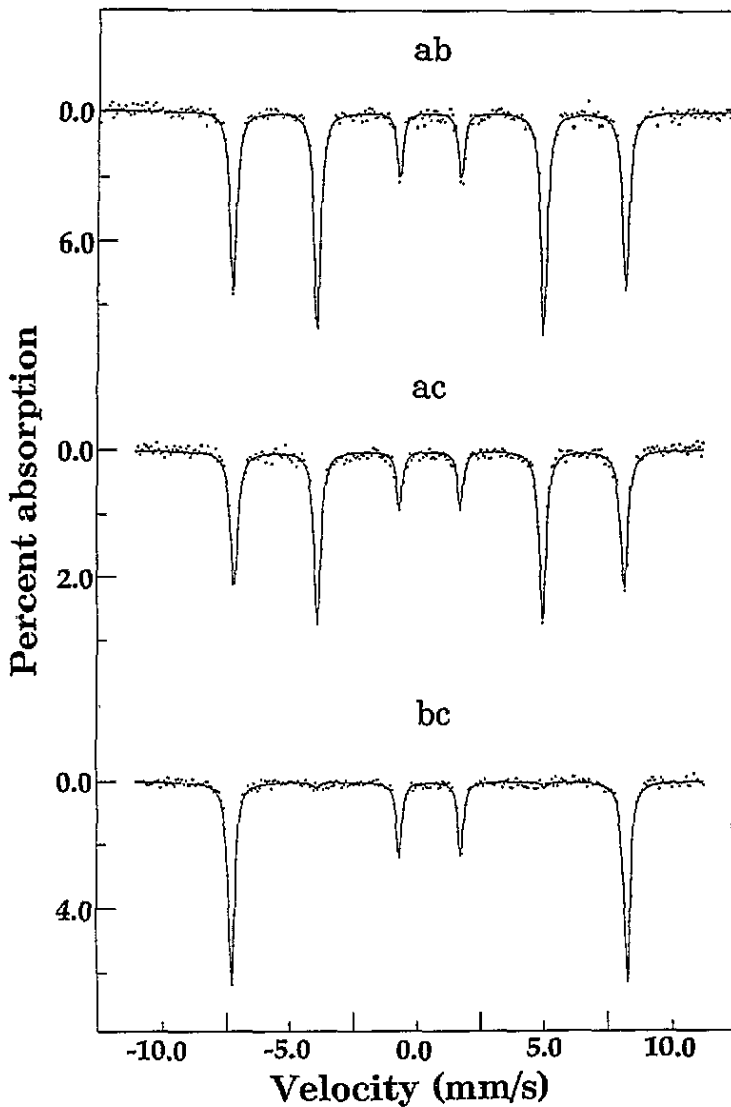


Figure 2. Single-crystal spectra at 4.2 K. Here *ab*, for example, denotes an *ab*-plane absorber and  $\gamma$ -rays parallel to the crystal *c* axis.

The values of  $\eta$  in table 2 are based on the crystal *b* axis being the *y* axis of the EFG PAS. According to the normal Mössbauer convention for labelling the EFG axes the *b* axis becomes the *x* axis for  $T \gtrsim 200$  K.

#### 4. Applied-field spectra at 4.2 K

The experiments were conducted in transverse geometry, i.e. with the applied field perpendicular to the  $\gamma$ -ray direction. The *ab*-plane absorber was oriented so that the external field was applied along the crystal *a* axis, this being the axis of alignment of the Fe spins in zero applied field.

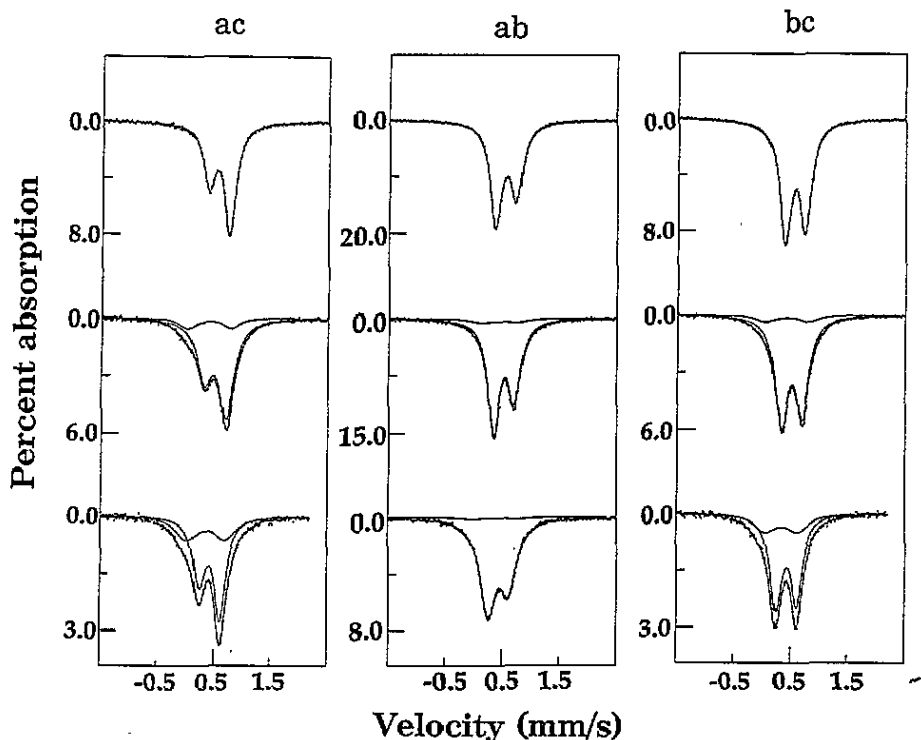


Figure 3. Some single-crystal spectra in the paramagnetic region: top, 20 K; middle, 100 K; bottom, 293 K.

Table 2. Values of  $\eta$  and  $\theta_a$  (angle between EFG  $z$  axis and the crystal  $a$  axis) at selected temperatures and deduced from spectra in the paramagnetic region respectively from  $ac$ -,  $bc$ - and  $ab$ -plane absorbers. The estimated errors are based on uncertainties in spectrum fitting and absorber alignment.

$T$ (K)	$\eta$ ( $\pm 0.10$ )	$\theta_a$ ( $\pm 5^\circ$ )	
20	0.18	52	49
100	0.13	52	48
200	0.01	51	48
293	-0.08	52	48

Some of the spectra, fitted in a standard manner in terms of the Mössbauer spectral parameters, are shown in figure 4. At low fields there are two sextets due to the addition/subtraction of the applied field  $B_{app}$  to the oppositely directed hyperfine fields from the two sublattices. At  $B_{app} \gtrsim 1.7$  T the Fe spins 'flop' to the  $c$  axis as shown by the zero 2, 5 line intensity, and a single effective field results from the vector addition of applied and hyperfine fields. The mid-point of the transition is at  $B_{SF} \approx 1.74$  T, slightly larger than the value of  $B_{SF} = 1.6$  T at 4.2 K in the phase diagram of O'Connor *et al* [6].

The transition is clearly very fast and presumably first-order, indicating that  $Rb_2FeCl_5 \cdot H_2O$  is a pure antiferromagnet. The spectra in the transition region were fitted on the basis of the coexistence of unflopped and flopped phases and the progress of the

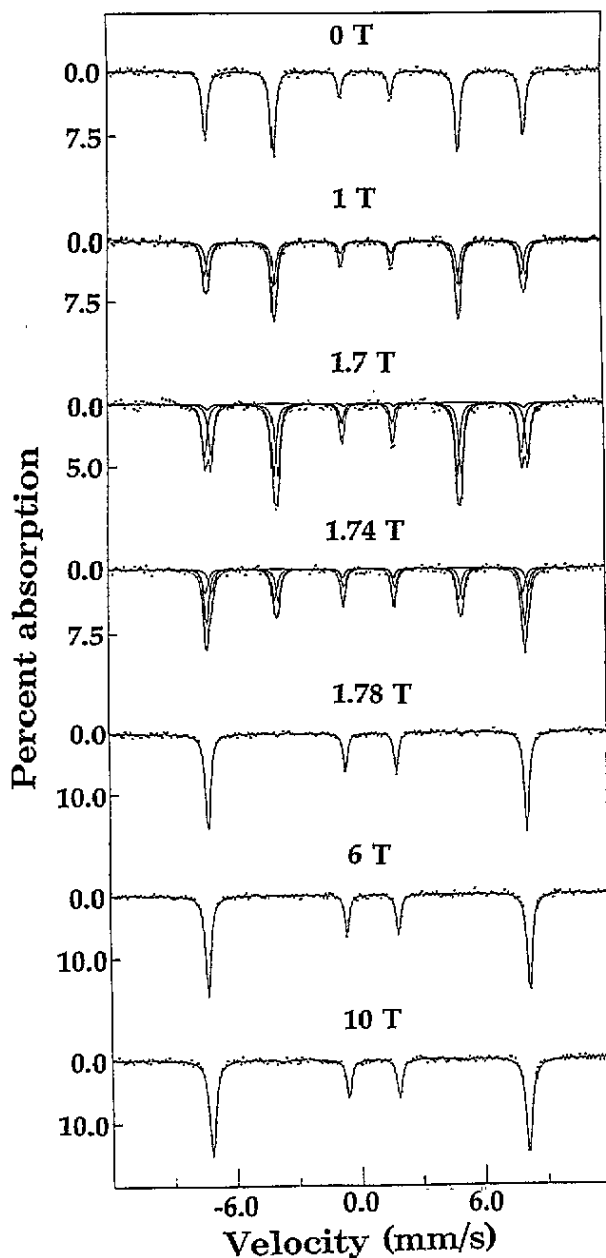


Figure 4. Some spectra taken with an *ab*-plane absorber with an applied field parallel to the *a* axis. The  $\gamma$ -ray direction is parallel to the *c* axis.

transition is shown in figure 5. The data show a small hysteresis effect. According to spin-wave theory  $\Delta B_{SF} = B_{SF} B_A / B_E$  where  $B_A$  and  $B_E$  are the anisotropy and exchange fields. Taking values for  $B_A$  and  $B_E$  from [1] gives  $\Delta B_{SF} = 0.006$  T, close to the measured value. The sharpness of the transitions with apparent hysteresis in both the  $K_2FeCl_5 \cdot H_2O$  and  $Rb_2FeCl_5 \cdot H_2O$  cases confirms the uniqueness of  $(NH_4)_2FeCl_5 \cdot H_2O$  in this family; in

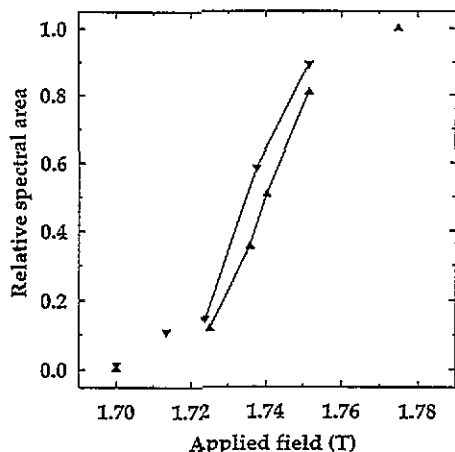


Figure 5. Fraction by absorption area of the spin-flopped phase in the transition region. ▲, increasing applied field; ▼, decreasing applied field. The lines are guides to the eye, linking points of the same sense in the middle of the transition region.

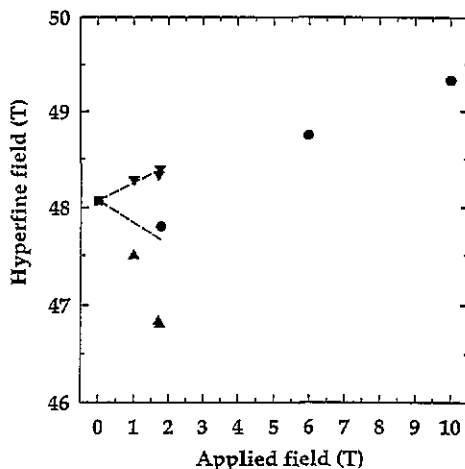


Figure 6. Variation of the magnetic hyperfine field: ▲▼ the two different  $B_{hf}$  from the two sublattices in the unflopped phase; ●  $B_{hf}$  in the flopped phase. The broken lines show the estimated first-order magnetization effect.

that case the spin reorientation was found to be continuous, i.e. a second-order transition.

The quadrupole shift changes abruptly at the spin-flop transition. At low applied fields and for the unflopped phase the average fitted  $2\varepsilon \approx -0.05 \text{ mm s}^{-1}$  in agreement with the powder sample data given in table 1. Now an expected shift may be calculated using the electrostatic parameters and  $\theta_a$  deduced from the paramagnetic spectra and the standard formulae

$$\Delta E_Q = e|V_{zz}| \frac{Q}{2} \left( 1 + \frac{1}{3}\eta^2 \right)^{1/2}$$

$$\varepsilon = eV_{zz} \frac{Q}{8} (3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi)$$

where  $\theta$ , and  $\phi$  are the polar angles in the EFG PAS of the magnetic field acting on the nucleus. Taking  $\theta = \theta_a = 50^\circ$  we thus calculate  $2\varepsilon = -0.06 \text{ mm s}^{-1}$ , in good agreement with the measured values. In the flopped phase the effective field acting on the nucleus is not quite along the  $c$  axis because of some small spin canting and the vector addition of the applied and hyperfine fields. However the angle to the  $c$  axis may be estimated to be  $5^\circ$  at most. Neglecting this and taking now  $\theta = 90^\circ - \theta_a = 40^\circ$  we may estimate  $2\varepsilon \approx -0.15 \text{ mm s}^{-1}$  in agreement with the average measured value of  $-0.18 \text{ mm s}^{-1}$  for the spin-flopped spectra. The consistency between calculated and measured quadrupole shifts for both the unflopped and flopped phases further verifies the determination of the EFG parameters from the paramagnetic spectra.

Figure 6 shows the variation of the magnetic hyperfine field with applied field. Below the spin-flop transition, the hyperfine fields from the two sublattices are unequal. This is due to a differential magnetization effect made measurable because the experimental temperature is a significant fraction of  $T_N$  so that the sublattice magnetizations are modified by the applied field. This is discussed fully in [5]. Suffice it to say that the effect here is again consistent with the theoretical estimate given in [5]. Above the spin-flop, the



magnitude of the time-average spin increases because of the increasing directional stiffness of the spins and this explains the increase in the hyperfine field. Ultimately the hyperfine field would be expected to fall again as the field-induced antiferromagnetic-paramagnetic transition is approached. However this transition is expected at  $B_{\text{app}} \approx 2B_E \approx 34$  T in the present case and it is therefore not surprising that the hyperfine field is still increasing at  $B_{\text{app}} = 10$  T.

## 5. Conclusions

The present work completes a set of Mössbauer spectroscopy experiments on three compounds  $A_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  with  $A = \text{NH}_4, \text{K}$  and  $\text{Rb}$ . These compounds are isostructural and also have similar cell dimensions. The programme was originally motivated by reports of unusual properties of  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ . In all three cases there existed previously a certain amount of powder sample Mössbauer measurements. We have extended these but we have been mainly concerned to obtain—for the first time in each case—single-crystal Mössbauer data.

There are certain similarities between the three: the orientation of the EFG PAS relative to the crystal axes, the  $a$  axis being the magnetic easy axis, and the spin reorientation to the  $c$  axis under application of an external field along the  $a$  axis. So far as Mössbauer measurements are concerned the principal differences between  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  and the other two compounds are as follows.

(i) The quadrupole splitting is temperature dependent, an effect previously ascribed to rotational motion of the  $\text{NH}_4$  ion [9].

(ii) The antiferromagnetic spectra indicate at least two magnetization curves and two ordering temperatures.

(iii) The field-induced spin reorientation is gradual rather than abrupt.

It seems now that these properties are indeed peculiar to the  $\text{NH}_4$  salt. The next steps would be to use other techniques—for example to detect any *small* canting of the Fe spin structure which may be responsible for (iii)—and to investigate other  $\text{NH}_4$ -containing antiferromagnets.

Although the  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  and  $\text{Rb}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  experiments were undertaken primarily to confirm the peculiar nature of  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  they are also notable for the observation of very sharp, possibly hysteretic spin-reorientation phase transitions.

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