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A Mössbauer study of $K_2FeCl_5 \cdot H_2O$

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Abstract. Mössbauer absorption spectra have been recorded for powder and single-crystal samples of the antiferromagnetic compound $K_2FeCl_5 \cdot H_2O$ over the temperature range 1.3–293 K and also at 4.2 K in applied magnetic fields up to 10 T. Details of the electrostatic hyperfine interaction have been deduced from the paramagnetic spectra. In the antiferromagnetic phase the spectra show the Fe spins to be aligned along the crystal a axis. An external field of 3.2 T reoriented the spins to the c axis. The observed spin reorientation phase transition was found to be very sharp, characteristic of a pure antiferromagnet. Comparisons are made with a recent study of $(NH_4)_2FeCl_5 \cdot H_2O$.

1. Introduction

The compounds $A_2FeX_5 \cdot H_2O$ (A = alkali or NH_4, X = halogen) are antiferromagnetic with low but easily accessible Néel temperatures $T_N \lesssim 25$ K. Their crystallographic and magnetic properties have been reviewed by Carlin and Palacio [1]. Recently Mössbauer spectroscopy measurements were made in this laboratory [2, 3] on $(NH_4)_2FeCl_5 \cdot H_2O$, a member of this family that has some unusual properties. For example, its low-temperature susceptibility data are not characteristic of a pure antiferromagnet and this had prompted the suggestion [4] of considerable canting of the Fe spins. This possibility was ruled out by the zero-field Mössbauer data [2]. However, the field-induced spin reorientation or 'spin flop' was found [3] to be a gradual rather than sudden transition, allowing the possibility of some *small* canting of the Fe spins. In this and other matters discussed in sections 3 and 4 it seemed desirable to have more detailed information on other compounds in this family to sharpen the comparison between them. Some Mössbauer data for $K_2FeCl_5 \cdot H_2O$ have been reported by Partiti *et al* [5] as part of a comparative study with $(NH_4)_2FeCl_5 \cdot H_2O$ but this work involved powder samples only. A large part of the present work concerns single-crystal measurements including spectra taken with applied magnetic fields.

2. Experimental details

Crystals of $K_2FeCl_5 \cdot H_2O$ were grown by evaporation from a 0.58:1 molar mix of KCl and $FeCl_3 \cdot 6H_2O$ dissolved in 2 M hydrochloric acid. The crystal growth habits were similar to those of $(NH_4)_2FeCl_5 \cdot H_2O$ reported by Brown and Hall [6] and the assignment of crystal axes was verified by x-ray diffraction. Single-crystal Mössbauer absorbers typically 25 mm^2 in area were prepared by setting crystals in low-temperature epoxy, thinning by abrasion to the optimum thickness for Mössbauer absorption experiments, and finally sealing with

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more epoxy. A powder sample of approximate thickness 35 mg cm^{-2} was prepared from ground crystals mixed with a similar mass of boron nitride.

Zero-field spectra were taken with a room-temperature spectrometer, a liquid-nitrogen spectrometer, a liquid-helium spectrometer with pumping facility for temperatures of 4.2 K and below, and a helium flow cryostat for temperatures in the 5–250 K range. In the latter case the sample temperature was measured using a calibrated carbon-glass resistor located in the sample mount. The applied-field spectra were taken at 4.2 K using a 10 T superconducting-magnet cryostat. The Mössbauer γ-ray sources were ^{57}Co/Rh and the constant-acceleration spectrometer drives were operated in double-ramp (flat-background) mode. In order to obtain good counting statistics with the single-crystal samples—against the poor counting geometry of the magnet spectrometer for example—spectrum run times were typically two days.

3. Zero-field spectra

3.1. Powder spectra

Examples of spectra are shown in figure 1. The instrumental linewidth throughout this work was typically 0.26 mm s^{-1}. Apart from the expected broadening at temperatures close to T_N the spectra were sharp and with no suggestion of the need for more than one component. This is in contrast with the $(NH_4)_2FeCl_5{\cdot}H_2O$ case where spectra in the antiferromagnetic region clearly required more than one fitted component [2, 5]. For brevity here the fitted parameters for only a few selected temperatures are given in table 1 and the temperature dependence of the magnetic hyperfine field is shown in figure 2. Above T_N the doublet spectra show a small quadrupole splitting, which is essentially independent of temperature. The value is in good agreement with the results of Partiti *et al* [5] as are also the values of the quadrupole shift and hyperfine field at 4.2 K, the one temperature below T_N in [5]. We see in table 1 that in the antiferromagnetic phase the quadrupole shift is small (i.e. $2|\epsilon| \ll \Delta E_Q$). This indicates a large angle between B_{hf} and the z axis of the electric-field-gradient principal-axes system (EFG PAS); we return to this point later.

Table 1. Mössbauer parameters from powder spectra at selected temperatures: centre shift δ relative to iron foil at room temperature, magnetic hyperfine field B_{hf}, quadrupole shift ϵ and quadrupole splitting ΔE_Q.

T (K)	δ (mm s^{-1})	B_{hf} (T)	2ϵ (mm s^{-1})	ΔE_Q (mm s^{-1})
1.3	0.53	50.4	−0.052	—
4.2	0.53	49.6	−0.051	—
10.1	0.54	40.0	−0.056	—
12.7	0.54	30.2	−0.051	—
17.9	0.54	—	—	0.21
293	0.42	—	—	0.21

3.2. Single-crystal spectra

Spectra were taken at various temperatures with three crystal orientations in *ab*-, *bc*- and *ac*-plane absorbers. The fitted Mössbauer parameters agreed with those obtained from the

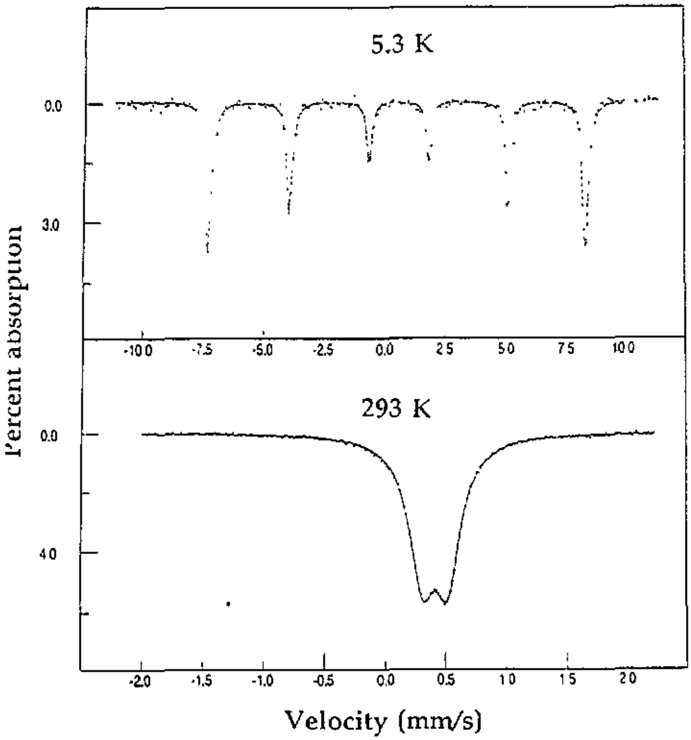

Figure 1. Powder spectra at 5.3 K and 293 K.

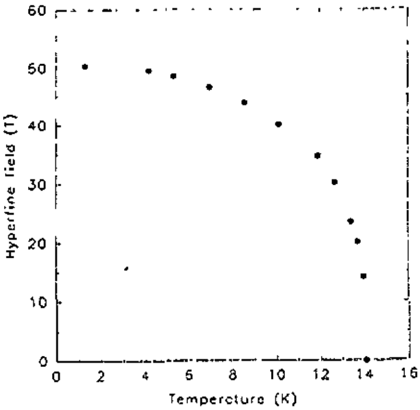

Figure 2. Temperature dependence of the magnetic hyperfine field. The collapse to zero B_{hf} is consistent with the ordering temperature T_N = 14.1 K reported in [1].

powder spectra and we therefore concentrate here on the orientational parameters of the hyperfine interaction, which may be deduced from the relative intensities of the absorption lines in the single-crystal spectra.

Spectra taken at 4.2 K are shown in figure 3. The absence of 2, 5 line intensity for the *bc*-plane absorber clearly shows that B_{hf} is closely parallel to the *a* axis; this is confirmed

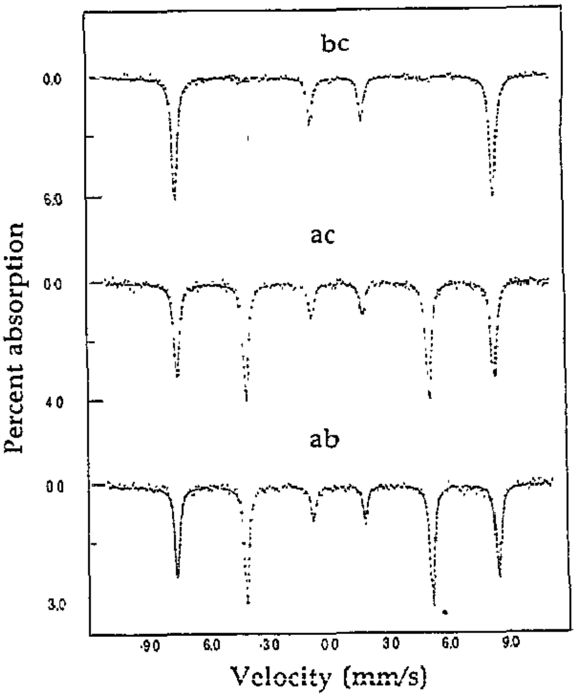

Figure 3. Single-crystal spectra at 4.2 K. Here *ab*, for example, denotes the use of an *ab*-plane absorber and γ-rays parallel to the *c* axis.

by the approximately 3:4:1 intensity ratios for the other two absorbers. We conclude that the Fe spins are aligned along the *a* axis, consistent with this being reported generally to be the magnetic easy axis for chloride members of this family of compounds [1].

As already noted, the quadrupole splitting is small so that the relative intensity of the doublet lines in the paramagnetic region is difficult to determine accurately. We were nevertheless able to obtain useful results and make a sensible comparison with the $(NH_4)_2FeCl_5{\cdot}H_2O$ case by taking well defined spectra at 20 K, 77 K and room temperature, some of these being shown in figure 4. To fit these we used a program based on the calculations of Kündig [7] in which spectra are computed as a function of hyperfine interaction parameters and γ-ray direction. EFG parameters were deduced using the procedure described in [2]. Briefly, on the hypothesis that the *b* axis is one of the EFG principal axes, the *ac*-plane absorber data may be used to determine the asymmetry parameter η; with this value of η either of the other two spectra (at a given temperature) may be used to determine the orientation of the other two EFG axes in the *ac* plane, thus also providing a consistency check. In summary we found V_{zz} to be negative, the crystal *b* axis to be the *y* axis of the EFG PAS—both results as in the $(NH_4)_2FeCl_5{\cdot}H_2O$ case—and values for η and θ_a as given in table 2. Here θ_a is the angle in the *ac* plane between the *z* (major) axis of the EFG PAS and the crystal *a* axis. The values of θ_a from the two different absorbers are in satisfactory agreement. Also, using the standard formulae

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

$$\epsilon = eV_{zz}\tfrac{1}{8}Q\left(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi\right)$$

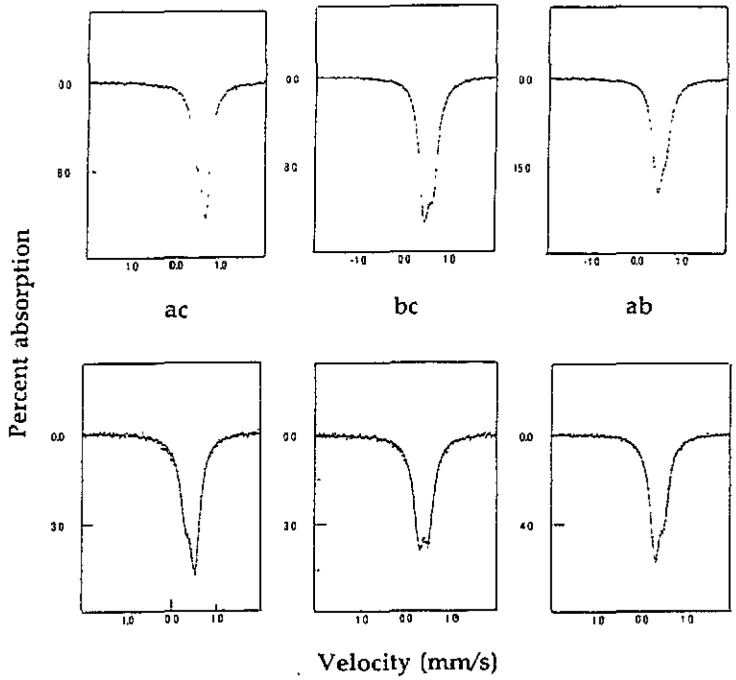

Figure 4. Some single-crystal spectra in the paramagnetic region: top, 20 K; bottom, 293 K.

with $\eta = 0.66$ and taking from table 1 an average $2\epsilon = -0.053$ mm s^{-1} from the antiferromagnetic spectra, we calculate an angle of $\theta = 52°$ between the z axis and the magnetic hyperfine field. Since the latter has been shown to be along the a axis this angle is just θ_a and further confirms our results.

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

	η ±0.1	θ_a(°) ±5	
20 K	0.6(6)	50	57
293 K	0.4(1)	57	55

We may conclude that $\theta_a \simeq 55°$, very similar to the value in the $(NH_4)_2FeCl_5{\cdot}H_2O$ case [2]. Also as in the latter case this means that the EFG z axis is not quite aligned with the Fe–O bond line which is at 40° to the a axis in $K_2FeCl_5{\cdot}H_2O$ and 41° in $(NH_4)_2FeCl_5{\cdot}H_2O$ [4]. In [2] we allowed the possibility of the NH_4 ion being partly responsible for the z axis not being collinear with the Fe–O bond line but the present work indicates that it is entirely due to asymmetry about this line in the position and bonding of Cl ions.

The low-temperature value of the asymmetry parameter is approximately the same as the $\eta \simeq 0.6$ deduced [2] for $(NH_4)_2FeCl_5{\cdot}H_2O$. In [2] we found η to decrease at higher temperature, falling to $\eta \simeq 0.1$ at room temperature, and had ascribed this behaviour to the hindered-rotor nature of the NH_4 ion, which is reportedly responsible for the temperature dependence of the quadrupole splitting [5]. On these grounds we might expect little temperature dependence of η in the present case. Our spectra at 77 K (not shown) were similar to those at 20 K but the 293 K data suggest some reduction in the value of η, although not as much as that in the $(NH_4)_2FeCl_5{\cdot}H_2O$ case. Because of the small separation of the doublet lines we cannot confidently be more definite about the possible temperature dependence of η in $K_2FeCl_5{\cdot}H_2O$ but we shall pursue this point further in the work on a similar compound with a somewhat larger quadrupole splitting.

4. Applied-field spectra at 4.2 K

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

In a magnetically split ^{57}Fe Mössbauer absorption spectrum the 1, 6:2, 5:3, 4 line intensity ratio is $3{:}4\sin^2\theta/(1+\cos^2\theta){:}1$ where θ here is the angle between the γ-ray direction and the magnetic field acting on the nucleus. In an applied-field ($\boldsymbol{B}_{\mathrm{app}}$) experiment this is the effective field given by the vector addition

$$\boldsymbol{B}_{\mathrm{eff}} = \boldsymbol{B}_{\mathrm{hf}} + \boldsymbol{B}_{\mathrm{app}}$$

where the direction of $\boldsymbol{B}_{\mathrm{hf}}$ is determined by the Fe ion spin. In the case of an antiferromagnet with oppositely directed $\boldsymbol{B}_{\mathrm{hf}}$ from the two spin sublattices, the Mössbauer spectrum shows two sextets with slightly different B_{eff}, i.e. an effective-field splitting. A spin reorientation of the Fe spins may therefore be monitored in Mössbauer spectra by the effective-field splitting and by the relative line intensities.

4.1. Nature of the spin-reorientation transition

Some spectra are shown in figure 5. For $0 < B_{\mathrm{app}} < 3.15$ T the 2, 5 line intensity remains strong and the effective-field splitting between the two sextets increases with B_{app} while the Fe spins stay aligned along the *a* axis. For $B_{\mathrm{app}} > 3.25$ T both the 2, 5 line intensity and the effective-field splitting have dropped to zero; the spins are now aligned along the *c* axis following a field-induced spin reorientation or 'spin flop'. That the spins reorient $a \rightarrow c$ is similar to the $(NH_4)_2FeCl_5{\cdot}H_2O$ case but the speed of the transition is very different. In the $(NH_4)_2FeCl_5{\cdot}H_2O$ case the spins were found [3] to rotate gradually over a field range of at least 1 T, suggesting a small spin canting, which can be responsible for the phase transition being continuous (second order) rather than abrupt (first order). In the present case, however, a gradual rotation was not observed and instead the coexistence of flopped and unflopped phases was seen in spectra taken in the very narrow transition region.

The progress of the transition is shown in figure 6, where the fraction by spectral absorption area of the flopped phase is plotted over a small range of applied field. The mid-point of the spin-flop transition is at $B_{\mathrm{SF}} \simeq 3.2$ T, slightly higher than the value of $B_{\mathrm{SF}} \simeq 2.8$ T at 4.2 K in the phase diagram of Palacio *et al* [8]. Theoretically the spin-flop phase transition in a pure antiferromagnet is first order, demonstrated by transition sharpness, phase coexistence and possibly hysteresis. We therefore also looked for the latter. The data in figure 6 do allow the possibility of a small difference $\Delta B_{\mathrm{SF}} \simeq 0.01$ T between the values with field increasing and decreasing. According to spin-wave theory $\Delta B_{\mathrm{SF}} = B_{\mathrm{SF}}B_{\mathrm{A}}/B_{\mathrm{E}}$ where B_{A} and B_{E} are respectively the anisotropy and exchange fields. Using the values

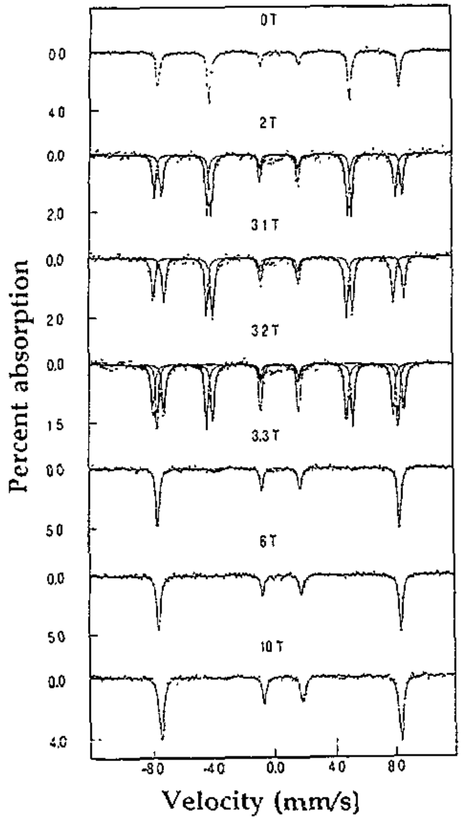

Figure 5. Some of the spectra taken with an *ab*-plane absorber with increasing applied fields. The applied field is along the *a* axis and the γ-ray direction is along the *c* axis. Note the coexistence of single- and double-sextet components at 3.2 T.

$B_A = 0.17$ T and $B_E = 20$ T reported [1] for $K_2FeCl_5{\cdot}H_2O$ this gives $\Delta B_{SF} = 0.03$ T, a small effect but larger than that observed.

The circled point in figure 6 suggests a larger observed hysteresis. It was taken with the field decreasing in the initial measurement cycle taken in coarse steps and the absorber had been in high field for several days. The other field-decreasing points in the 3.15–3.25 T range are from a later finely-spaced sequence in the transition region only, before which the field was taken up high and down again in a time of little over an hour. Although it would have been easy to omit this point as the result of error or instrumental effect we record it with the tentative remark that dwell time in high field may have some role in magnetic history. Although it would be very expensive in spectrometer time we intend to pursue this point further if the effect recurs in work on a similar compound presently under way.

According to mean-field theory, however, it is somewhat surprising to see even the possibility of hysteresis emerging in our data and it has so far not been detected in other similar fast spin-flop transitions. A small misalignment between the easy axis and the applied field may change an inherently first-order transition into a second-order one. The angle required is $\tan^{-1}(B_A/2B_E) \simeq 0.25°$ here, which is smaller than the uncertainty in experimental alignment. However, if the misalignment is only a few degrees the observed transition would still be fast and the coexistence of flopped and unflopped phases could

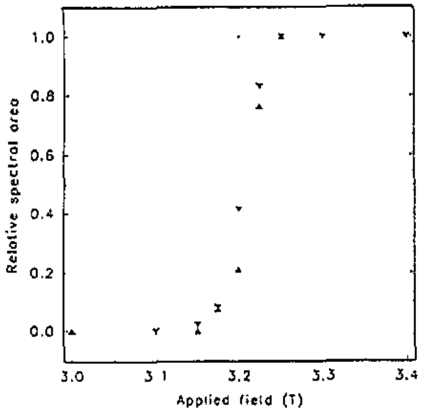

Figure 6. Variation of the fraction of absorption due to the spin-flopped phase in the transition region: ▲, increasing applied field; ▼, decreasing applied field; ◎, see text.

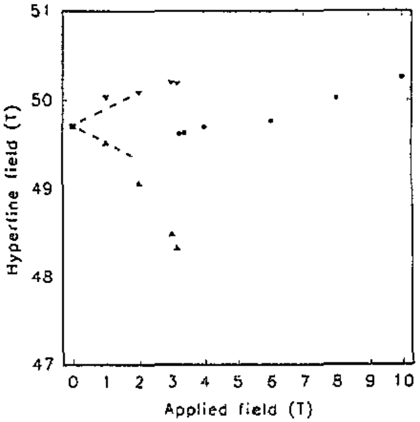

Figure 7. Variation of the hyperfine field with applied field: ▲, $B_{\mathrm{hf}}(S\uparrow)$; ▼, $B_{\mathrm{hf}}(S\downarrow)$; ●, B_{hf} in the flopped phase. The broken lines show the estimated theoretical magnetization effect for small applied fields.

therefore still arise because of a small variation of B_{SF} within the sample due to some inhomogeneity or strain. In summary, although the observation of hysteresis here is unproven, the spin-flop transition is undoubtedly very fast and almost certainly inherently first order.

4.2. *Quadrupole shift*

The quadrupole shift changes abruptly at the spin-flop transition. At low fields ($B_{\mathrm{app}} \leqslant 3.1$ T) in the unflopped phase the fitted $2\epsilon \simeq -0.05$ mm s^{-1} in agreement with the powder-sample data. At high fields (3.3 T $\leqslant B_{\mathrm{app}} \leqslant$ 10 T) in the flopped phase the average fitted $2\epsilon \simeq -0.14$ mm s^{-1} with no discernible trend. The change in 2ϵ is due, of course, to the change in angle between the effective field and the EFG z axis. Now in the flopped phase the effective field is not quite along the c axis because of two effects which act in mutual opposition: (i) canting by $\boldsymbol{B}_{\mathrm{app}}$ of the Fe spins and therefore $\boldsymbol{B}_{\mathrm{hf}}$ and (ii) the vector addition of $\boldsymbol{B}_{\mathrm{hf}}$ and $\boldsymbol{B}_{\mathrm{app}}$. The canting angle ϕ is given by both spin-wave and mean-field theory to be approximately $\sin^{-1}(B_{\mathrm{app}}/2B_{\mathrm{E}})$. We may therefore calculate that $\boldsymbol{B}_{\mathrm{eff}}$ is at an angle to the c axis of approximately 3° at $B_{\mathrm{app}} = 10$ T and, of course, at an even smaller angle at lower fields. Neglecting this angle and therefore taking the angle between $\boldsymbol{B}_{\mathrm{eff}}$ and z to be $90° - \theta_a \simeq 35°$ in the flopped phase, we calculate $2\epsilon \simeq -0.12$ mm s^{-1}, in reasonable agreement with the measured values and further confirming the earlier determination of the direction of the EFG z axis.

4.3. *Variation of the hyperfine field*

Figure 7 shows the variation of hyperfine field with applied field. Above the spin-flop field the single hyperfine field is deduced from the fitted effective field by vector addition:

$$B_{\mathrm{hf}} = B_{\mathrm{app}} \sin\phi + \left(B_{\mathrm{eff}}^2 - B_{\mathrm{app}}^2 \cos^2\phi\right)^{1/2}.$$

Below the spin-flop field the addition is simply arithmetic: $B_{\mathrm{hf}} = B_{\mathrm{eff}} - B_{\mathrm{app}}$ for the sextet with the larger B_{eff} and $B_{\mathrm{hf}} = B_{\mathrm{eff}} + B_{\mathrm{app}}$ for the smaller B_{eff}. We see that these two hyperfine fields from the two oppositely directed sublattice spins are unequal. Following the notation used in [3] $S\uparrow$ now denotes the spins for which $B_{\mathrm{eff}} > B_{\mathrm{hf}}$ and $S\downarrow$ similarly the spins for which $B_{\mathrm{eff}} < B_{\mathrm{hf}}$. We find $B_{\mathrm{hf}}(S\uparrow) < B_{\mathrm{hf}}(S\downarrow)$; experimentally this means that the effective-field splitting is less than $2B_{\mathrm{app}}$.

Now in the analysis of the $(NH_4)_2FeCl_5 \cdot H_2O$ data [3] it was found necessary to allow unequal hyperfine fields to obtain satisfactory fits to the spectra in the reorientation region; it was suggested that this was due to a differential magnetization effect of the applied field. This could not be established conclusively because of the complexity arising in that case from the greater number of spectral components and from the reorientation being gradual and starting at low applied fields. In these respects the present case is much clearer because of the simpler spectra and because the Fe spins stay aligned with the applied field up to the sharp spin-flop transition. We are thus able to confirm the magnetization effect, which arises in the following way. The temperature (4.2 K) is a significant fraction of $T_{\mathrm{N}} \simeq 14$ K so that the sublattice magnetization is not saturated and may therefore be changed slightly by the applied field. Now through the dominant Fermi contact term the hyperfine field is proportional to the sublattice magnetization and opposite in direction to it. Thus the sublattice spins $S\uparrow$, whose time-average spins give a hyperfine field in the same direction as the applied field, have a magnetization that is in the opposite direction and therefore reduced by the applied field. Hence $B_{\mathrm{hf}}(S\uparrow) < B_{\mathrm{hf}}(S\downarrow)$ as observed.

The magnitude of the effect may be understood as follows. Using mean-field theory and the proportionality between magnetization and hyperfine field it may be shown that for small applied fields we have approximately

$$\lim_{B_{\mathrm{app}}\to 0}\left(\frac{\partial B_{\mathrm{hf}}}{\partial B_{\mathrm{app}}}\right)_T \simeq \pm\frac{T}{B_{\mathrm{E}}}\left(\frac{\partial B_{\mathrm{hf}}}{\partial T}\right)_{B_{\mathrm{app}}=0}.$$

Taking an approximate value for the last quantity above at 4.2 K from the data of figure 2, we are able to estimate roughly the first-order effect of the applied field and this is represented by the two lines drawn through the $B_{\mathrm{app}} = 0$ point in figure 7. It is not possible to measure accurately the effect for $B_{\mathrm{app}} \leqslant 1$ T because the two sextets are then not resolved, but the trend of the existing data does not contradict the theoretical estimate. For higher applied fields (1 T $< B_{\mathrm{app}} <$ 3 T) departure from the first-order estimate is expected and observed. $B_{\mathrm{hf}}(S\uparrow)$ decreases faster than $B_{\mathrm{hf}}(S\downarrow)$ increases because the latter is closer to saturation. In addition, as the spin flop is approached the spins lose directional rigidity, further enhancing the magnetization-effect difference between $B_{\mathrm{hf}}(S\uparrow)$ and $B_{\mathrm{hf}}(S\downarrow)$. Above the spin flop, as is already known [9], the spins recover directional rigidity with increasing applied field; thus the time-average spin increases again and accordingly so does the hyperfine field.

A practical point arising from the differential magnetization effect is worth noting. In the study of field-induced continuous spin reorientation with the Mössbauer technique, the effective-field splitting is sometimes used as a measure of the spin rotation angle. This is quite satisfactory if the experimental temperature is a small fraction of the ordering temperature but otherwise inaccurate results would be obtained.

5. Conclusions

The data taken with powder samples of $K_2FeCl_5 \cdot H_2O$ agree very well with a previously published report and we have concentrated here on the further information derived from single-crystal absorbers. Despite the small quadrupole splitting we were able to deduce parameters of the hyperfine electrostatic interaction from spectra taken in the paramagnetic region. The orientation of the EFG PAS relative to the crystal axes is similar to that for $(NH_4)_2FeCl_5{\cdot}H_2O$. The asymmetry parameter is also similar at low temperature but has a smaller temperature dependence. The deduced EFG parameters correctly reproduce the small quadrupole shifts observed in the magnetically split spectra in both the antiferromagnetic and spin-flopped phases. Spectra taken at 4.2 K show the spins to be aligned along the a axis. An external field applied along this easy axis reorients the spins to the c axis. The spin reorientation at 3.2 T is very fast and phase coexistence was observed, indicative of a first-order phase transition possible with a pure antiferromagnet. This is in marked contrast to the $(NH_4)_2FeCl_5{\cdot}H_2O$ case. The recent suggestion of an applied-field differential magnetization effect on the hyperfine fields in an antiferromagnet has been verified.

Acknowledgments

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