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## Mössbauer spectra from $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ in applied magnetic fields

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**Abstract.** Mössbauer absorption spectra have been recorded for single-crystal samples of the antiferromagnetic compound  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  in applied magnetic fields up to 10 T. A reorientation of the Fe ion spins from the crystal  $a$  axis to the  $c$  axis was observed. This transition was found to be a continuous and planar rotation at fields around 2 T. Detailed fitting of the spectra in the spin-reorientation region indicated some inequality between the magnetic hyperfine fields associated with oppositely directed ionic spins.

### 1. Introduction

The compounds  $\text{A}_2\text{FeX}_5 \cdot \text{H}_2\text{O}$  ( $\text{A}$  = alkali or  $\text{NH}_4$ ,  $\text{X}$  = halogen) are antiferromagnetic with readily accessible Néel temperatures  $T_N$  in the 5–25 K range. The particular compound  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  is quite unusual in some of its reported properties. McElearney and Merchant [1] found two closely spaced heat capacity cusps in the region of  $T_N \simeq 7$  K; they also reported magnetic susceptibility data not characteristic of a pure antiferromagnet. In previous Mössbauer spectroscopy measurements on powder samples Partiti *et al* [2] and Calage *et al* [3] found that in the antiferromagnetic region their spectra could not be satisfactorily fitted with just one magnetic hyperfine field.

We recently reported [4] a Mössbauer study of  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  over the temperature range 1.5–290 K using various powder and single-crystal absorbers. In the antiferromagnetic region we showed that the spectra could satisfactorily be fitted with a small number of components together with relaxation broadening near  $T_N$  attributed to critical fluctuations. We found that the Fe spins were aligned along or close to the crystal  $a$  axis and not, as had previously been suggested in view of the susceptibility data [1], canted at a large angle to this axis. Our data also suggested the possibility of two slightly different ordering temperatures which may be responsible for the two heat capacity cusps. It had earlier been conjectured that the lower-temperature cusp might arise from a spin-reorientation phase transition but our data showed no evidence of such a transition.

In the present article we report a further study of this compound in its antiferromagnetic phase, specifically the spin reorientation (SR) induced by applied magnetic fields.

## 2. Experimental details

Single-crystal samples of area approximately 25 mm<sup>2</sup> were prepared for Mössbauer absorption experiments as described earlier [4]. Both *ab*- and *ac*-plane absorbers were used.

Mössbauer spectra were taken at 4.2 K using a 10 T superconducting-magnet cryostat. The absorbers were oriented such that the applied field was along the crystal *a* axis, this being the axis of alignment of the Fe spins in zero applied field as mentioned earlier. The experiments were conducted in transverse geometry, i.e. applied field perpendicular to the  $\gamma$ -ray direction. Thus for the *ab*-plane absorber the  $\gamma$ -rays were along the *c* axis and, for the *ac*-plane absorber, along the *b* axis. The  $\gamma$ -ray sources were <sup>57</sup>Co/Rh and the constant-acceleration spectrometer drive was operated in double-ramp (flat-background) mode.

## 3. Results and discussion

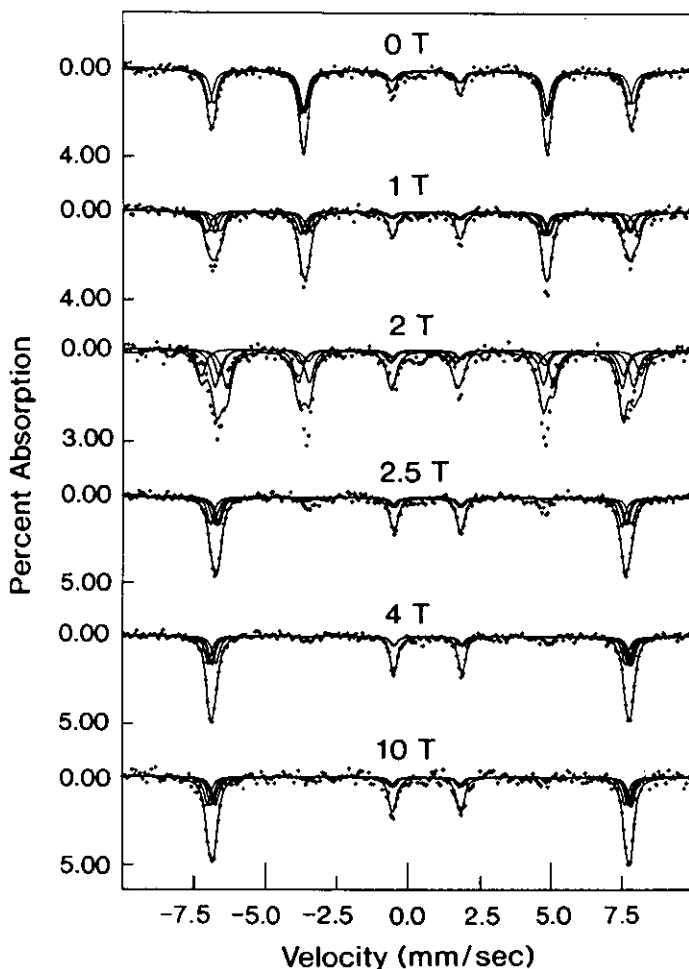
In a magnetically split (six-line) Mössbauer absorption spectrum the 1,6:2,5:3,4 line intensity ratio is  $3:4\sin^2\theta/(1 + \cos^2\theta):1$  where  $\theta$  is the angle between the  $\gamma$ -ray direction and the magnetic field acting on the nucleus. In a zero-field experiment this is just the hyperfine field  $B_{\text{hf}}$  whose direction is determined by the Fe ion spin. In an applied-field ( $B_{\text{app}}$ ) experiment the nucleus senses an effective field

$$B_{\text{eff}} = B_{\text{hf}} + B_{\text{app}}$$

and, in the case of an antiferromagnet with equal and opposite  $B_{\text{hf}}$  from the two sublattices, the Mössbauer spectrum shows two sextets with slightly different  $B_{\text{eff}}$ . This effective-field splitting is also dependent on the orientation of the Fe spins through the above vector addition. In the study of field-driven SR the two effects of line intensity and effective-field splitting may be incorporated into one computational model for spectrum fitting. For this we have used a model similar to that of Kündig [5] in which line positions and intensities are computed as a function of the electric and magnetic hyperfine interaction parameters and the relative orientations of  $B_{\text{hf}}$ ,  $B_{\text{app}}$ ,  $\gamma$ -ray direction, and the electric-field-gradient principal axes system. For  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  at 4.2 K the electric quadrupole interaction has a relatively small but not negligible effect on line positions and its parameters were taken to be those determined just above  $T_N$  in [4].

In previous (zero-field) Mössbauer experiments [2–4] it was found that spectra in the antiferromagnetic region could not be satisfactorily fitted with just one magnetic hyperfine field component. In [4] we used as many as four closely-spaced components but could not rule out the possibility of two being sufficient with a somewhat different model of relaxation line broadening. Since the submission of [4] Misra and Li [6] have reported an EPR study of Fe<sup>3+</sup>-doped  $(\text{NH}_4)_2\text{InCl}_5 \cdot \text{H}_2\text{O}$  observing two magnetically inequivalent Fe<sup>3+</sup> ions. In the present work the spectra have been analysed on the basis of two zero-applied-field components, giving four sextets with an applied field. The basis of four zero-field components might improve the fits somewhat but would not affect the main conclusions to be drawn.

Figure 1 shows examples of spectra taken with an *ab*-plane absorber. The line intensity ratio goes from approximately 3.4:1 at zero field, the Fe spins being aligned



**Figure 1.** Some Mössbauer spectra from an *ab*-plane absorber. The applied field is along the *a* axis and the  $\gamma$ -ray direction is along the *c* axis. The basis of the fits is equal and opposite hyperfine fields rotating in the *ac* plane.

initially along the *a* axis, to 3:0:1 at high field. The spins clearly reorient to the *c* axis, as has also been observed [7] for the 'spin flop' in the similar compound  $\text{Cs}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$ . Correspondingly the field splitting initially increases with  $B_{\text{app}}$  and then decreases as the spins and  $B_{\text{hf}}$  rotate away from the *a* axis. We have already shown [4] that there is very little canting of the spins from the *a* axis at zero field; the high-field spectra here show that there is also very little canting of the spins from the *c* axis in the spin-flopped phase.

The data also indicate that the SR is a rotation more gradual than in the  $\text{Cs}_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  case [7] where the SR at  $B_{\text{app}} = 1.3$  T takes place over a field range of approximately 0.05 T, implying in that compound a first-order (sudden) phase transition. Here, it was not possible to fit the  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  spectra on the basis of a first-order transition with the coexistence of flopped and unflopped phases in the SR region.

We therefore fitted the spectra on the basis of a continuous transition. However, initial fits on this basis were not very satisfactory in the middle of the SR region around  $B_{\text{app}} = 2$  T, as may be seen in figure 1. The best-fit field splitting is too large and wanting a larger rotation angle and is therefore incompatible with the 2,5 line intensity which is too small and wanting a smaller rotation angle. These particular fits, using the general model described earlier, included the constraints that the two  $B_{\text{hf}}$  from each spin pair are equal and opposite and that all  $B_{\text{hf}}$  lie in the  $ac$  plane. Removing the requirement of opposite  $B_{\text{hf}}$  (i.e. allowing some spin canting) in the SR region did not significantly improve the fits. The incompatibility between line intensity and field splitting may theoretically be relieved by allowing the Fe spins to move out of the  $ac$  plane during the SR; any movement of the spins away from the  $a$  axis would reduce the field splitting but such a movement towards the  $b$  axis would also maintain 2,5 line intensity. Improved fits were made in this way, the Fe spins moving approximately  $40^\circ$  out of the  $ac$  plane in the course of the  $a \rightarrow c$  SR. (Non-planar SR is not unknown; it has been reported, for example, by Nikolov *et al* [8] for  $\text{HoFeO}_3$ .) To test this possibility we used an  $ac$ -plane absorber. In this case the line intensity ratio should remain 3:4:1 throughout if the Fe spins rotate in the  $ac$  plane; otherwise there would be a dip in the 2,5 line intensity in the SR region. This intensity, deduced directly from the spectra rather than from fits, is plotted in figure 2. These data would admit only a small movement of the Fe spins out of the  $ac$  plane and certainly not enough to be consistent with the fitting of the  $ab$ -plane absorber data on the basis of a non-planar SR.

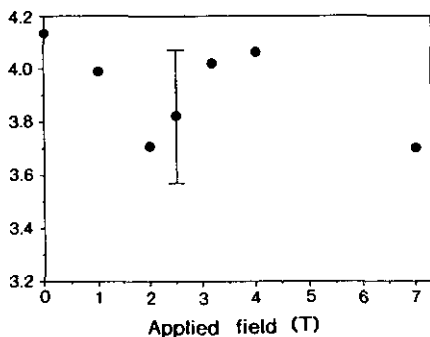


Figure 2. Relative intensity of the 2,5 lines in spectra from an  $ac$ -plane absorber.

By elimination we were therefore led to relax the constraint that the two opposite  $B_{\text{hf}}$  from a spin pair are equal. Hereon  $S \uparrow$  denotes a spin for which the vector addition of  $B_{\text{hf}}$  and  $B_{\text{app}}$  gives  $B_{\text{eff}} > B_{\text{hf}}$  and  $S \downarrow$  similarly a spin which gives  $B_{\text{eff}} < B_{\text{hf}}$ . Then if  $B_{\text{hf}}(S \uparrow) < B_{\text{hf}}(S \downarrow)$  the effective-field splitting is reduced.

Thus the  $ab$ -plane absorber spectra were finally fitted on the basis of four independent values of  $B_{\text{hf}}$  from the two spin pairs, these being constrained to rotate in the  $ac$  plane. The two rotation angles (one for each spin pair) were also allowed to be independent in the procedure but the fits gave angles which were not significantly different, consistent with the spin pairs rotating in unison. In the final analysis we allowed for differences between the four sextets in the perturbation of line positions due to the quadrupole interaction. The  $z$  and  $x$  axes of the electric-field-gradient tensor lie in the  $ac$  plane [4], the  $z$  axis being at  $\pm 50^\circ$  to the crystal  $a$  axis. The directions of the  $z$  and  $x$  axes are local, alternating through the crystal structure (there being four Fe sites per unit cell) and so individual spins may rotate through

either the  $z$  axis or the  $x$  axis. All combinations for the four spins were tried, the best fits being with one  $S \uparrow$  spin rotating through the  $z$  axis and the other  $S \uparrow$  spin rotating through the  $x$  axis and similarly for the two  $S \downarrow$  spins. Final fits on this basis for spectra in the SR region are shown in figure 3. The deduced  $B_{\text{hf}}$  are shown in figure 4; on the average, these show some reduction in the SR region as expected [9].

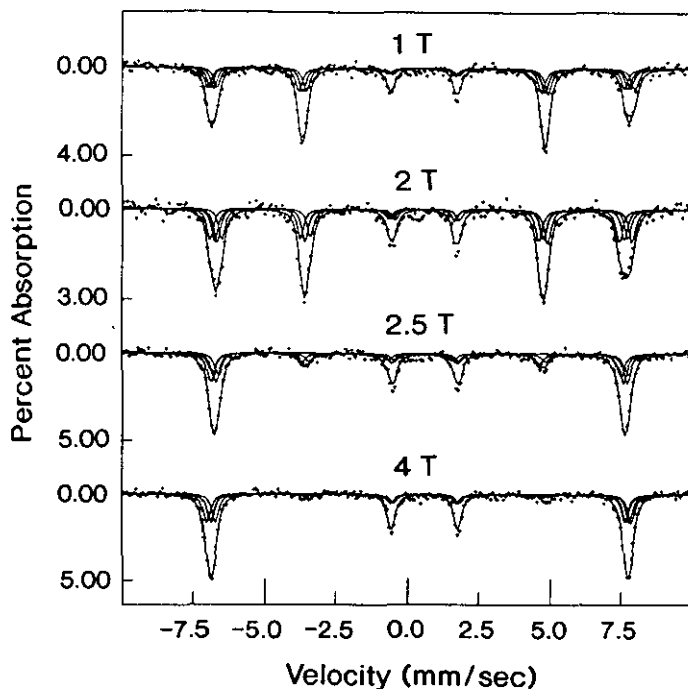


Figure 3. Final fits as described in the text to spectra in the spin-reorientation region.

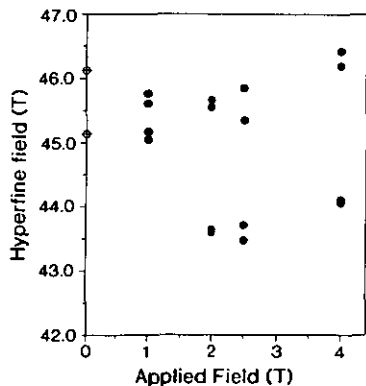


Figure 4. Hyperfine fields  $B_{\text{hf}}$  in the spin-reorientation region from fits shown in figure 3. For any particular applied field the two lower  $B_{\text{hf}}$  are for  $S \uparrow$  spins ( $B_{\text{eff}} > B_{\text{hf}}$ ) and the two higher  $B_{\text{hf}}$  are for  $S \downarrow$  spins ( $B_{\text{eff}} < B_{\text{hf}}$ ).

The reason for some small inequality between the hyperfine fields of a pair of antiferromagnetically coupled spins might be thought to be due to a difference in the contribution of the dipolar field to the hyperfine field as the spins rotate. However, the

dipolar field has a geometric relation to the electric quadrupole interaction whereas our analysis indicates that the difference is to do with the directions of the spins ( $S \uparrow$  versus  $S \downarrow$ ) rather than whether they rotate through the  $z$  or  $x$  axes. This suggests instead a magnetization effect, perhaps made measurable because the low  $T_N \approx 7$  K means that the sublattice magnetizations are some way from saturation at 4.2 K. Through the dominant Fermi contact term in the hyperfine field the latter is opposite in direction to the ion moment and a small difference between the magnetization of the  $S \uparrow$  and  $S \downarrow$  spins due to an applied field would give  $B_{\text{hf}}(S \uparrow) < B_{\text{hf}}(S \downarrow)$  as observed.

In [4] we acknowledged that we could not rule out some small canting of the Fe spins and that this may be responsible for the unusual susceptibility data [1]. Here we have seen that spin canting is not of itself sufficient to give good fits to the SR spectra but again we do not rule it out. Indeed spin canting is a possible cause of a SR being continuous rather than sudden and this is what we have observed in the present work.

#### 4. Conclusions

We have studied field-driven spin reorientation at 4.2 K in  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  using Mössbauer spectroscopy and  $ab$ - and  $ac$ -plane single-crystal absorbers. As in  $\text{Cs}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  the Fe spins reorient from the  $a$  axis to the  $c$  axis. Unlike in the  $\text{Cs}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  case, the reorientation transition is gradual rather than sharp, suggesting the possibility of some small canting of the Fe spins from a purely antiferromagnetic configuration; this may also explain the unusual low-temperature susceptibility data for  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ . The reorientation has been shown to be essentially a planar rotation. In the course of this rotation there appears to be a small inequality in the hyperfine fields of the antiferromagnetically coupled spins.

#### Acknowledgment

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