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1992 J. Phys.: Condens. Matter 4 9191

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A Mössbauer study of $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$

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Received 4 June 1992, in final form 4 September 1992

Abstract. Mössbauer spectra of $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ have been measured over the temperature range 1.5–297 K for powder and various single-crystal absorbers. This antiferromagnet has shown complicated magnetic behaviour but, contrary to a previous suggestion, our spectra show that below the ordering temperature the Fe spins are aligned along the a axis. The antiferromagnetic spectra may be fitted with a small number of components coupled with relaxation broadening due to critical fluctuations. The data suggest two closely spaced ordering temperatures. Details of the hyperfine electrostatic interaction have been deduced from the paramagnetic spectra. No evidence was found for a reported structural phase change in the paramagnetic region.

1. Introduction

The compounds $\text{A}_2\text{FeX}_5 \cdot \text{H}_2\text{O}$ ($\text{A} = \text{alkali or } \text{NH}_4$, $\text{X} = \text{halogen}$) are antiferromagnetic with Néel temperatures in the 5–25 K range. Their crystallographic and magnetic properties have been reviewed by Carlin and Palacio [1]. With few exceptions e.g. $\text{Cs}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ they belong to the space group $Pnma$ and generally the crystal a axis is the magnetic easy axis. The crystal structure is shown in figure 1.

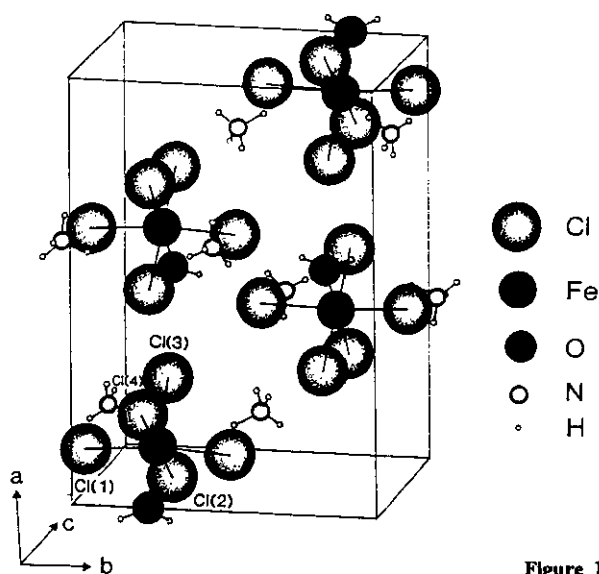


Figure 1. The structure of $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$.

The $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ compound is particularly interesting for a number of reasons. McElearney and Merchant [2] found two closely spaced heat capacity cusps: one at $T = 7.25$ K presumably associated with the magnetic ordering at T_N and a lower one at $T = 6.87$ K which was thought possibly to be due to a spin reorientation phase transition. McElearney and Merchant [2] also measured the magnetic susceptibility from 1.5–30 K. Their data below T_N indicated that the Fe spins lie in the ac plane but, since no easy axis was found, they concluded that the spins have a canted structure. On the grounds that there was little difference between χ_a and χ_c it was further suggested that the spins are canted at nearly 90° to each other, possibly due to them being aligned nearly parallel to the Fe–O bonds.

Mössbauer spectroscopy measurements have been reported by Partiti *et al* [3] and Calage *et al* [4]. Above T_N Partiti *et al* found that the spectra were sharp doublets with a quadrupole splitting temperature dependence which they ascribed to thermally activated reorientations of the NH_4^+ ion. Below T_N they found that their sextet spectra could not be very satisfactorily fitted with a single magnetic hyperfine field at any given temperature, an effect which had been noted earlier [5]. They were able to conclude, however, that the angle θ between the hyperfine field and the z principal axis of the electric-field-gradient (EFG) tensor was at least 33° . If this z axis is locally, as expected, close to the Fe–O axis (the Fe environment being five Cl^- ions and a water molecule) then this result contradicts the earlier suggestion of McElearney and Merchant [2] for the spin alignment. Calage *et al* [4] also found it necessary to use more than one spectral component to fit the antiferromagnetic spectra. The most notable feature of this work, however, is the reported structural phase change just above T_N held to be responsible for the paramagnetic spectrum showing a broad single line rather than a fairly well resolved doublet; the hysteresis in this supposed phase change was so large that the new phase remained on raising the temperature to room temperature.

In view of the reported peculiarities of this compound it seemed important to investigate it further and the present article includes, for the first time to our knowledge, Mössbauer spectroscopy measurements on single-crystal samples.

2. Experimental details

Crystals of $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ were grown by evaporation from a 1:1 molar mix of NH_4Cl and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 2 M hydrochloric acid. The crystal axes were determined by oscillation X-ray photography. Single-crystal Mössbauer absorbers (approximately 25 mm^2 in area) were prepared by setting crystals in low-temperature epoxy, abrading to produce platelets in the appropriate crystal planes, thinning by finer abrasion to the optimum thickness for Mössbauer absorption experiments, and finally sealing with more epoxy. Powder samples of thickness approximately 30 mg cm^{-2} were prepared from ground crystals mixed with a similar mass of boron nitride.

Mössbauer spectra were taken with two spectrometers: a continuous helium flow cryostat for temperatures above 4.2 K and a liquid helium cryostat with pumping facility for temperatures in the 1.5–4.2 K range. In the flow cryostat measurements, the sample temperature was monitored using a carbon–glass resistor located in the sample mount. At temperatures near to $T_N \simeq 7.3$ K, where the Mössbauer spectrum is most temperature-sensitive, the temperature stability and accuracy of relative temperatures was approximately ± 0.01 K, the absolute temperature measurement

having an uncertainty of approximately ± 0.1 K. The Mössbauer γ -ray sources were $^{57}\text{Co}/\text{Rh}$ and the constant-acceleration spectrometer drives were operated in double-ramp (flat background) mode.

3. Results and discussion

3.1. Powder spectra

Examples of spectra at various temperatures are shown in figure 2 and the fitted Mössbauer parameters are given in table 1. The spectra in the paramagnetic region could be fitted satisfactorily with one doublet component and, except near the ordering temperature, with a quite narrow linewidth. The measured values of the quadrupole splitting ΔE_Q are in excellent agreement with those of Partiti *et al* [3]. Close to the ordering temperature the doublet lines broadened somewhat; this may be due to critical fluctuations and we discuss this further in section 3.3. Despite repeated thermal cycling with different powder samples—and subsequently also with single-crystal samples—we did not see any evidence in our spectra of another phase as reported by Calage *et al* [4] and at the present time we have no explanation for this difference. The temperature dependence of the quadrupole splitting (shown in figure 4 with other parameters to be discussed in section 3.2) has been attributed by Partiti *et al* [3] to thermal activation of transitions between different orientations of the NH_4^+ ion. That NH_4^+ may be a hindered rotor in solids is well known and the reader may refer to Partiti *et al* [3] for a discussion of this effect.

Table 1. Mössbauer parameters from powder spectra at selected temperatures: centre shift δ relative to iron foil at room temperature, magnetic hyperfine field B , quadrupole shift ϵ , and quadrupole splitting ΔE_Q . The spectra in the antiferromagnetic region were fitted with linewidths $\Gamma - \Delta\Gamma$, Γ , $\Gamma + \Delta\Gamma$ outwards from the spectrum centre.

T (K)	δ (mm s ⁻¹)	B (T)	2ϵ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	Γ (mm s ⁻¹)	$\Delta\Gamma$ (mm s ⁻¹)
1.5	0.55	48.7	-0.31		0.29	0.02
	0.55	48.6	-0.02		0.28	0.02
4.2	0.54	44.4	-0.11		0.31	0.01
	0.55	43.3	-0.21		0.34	0.02
6.7	0.55	30.3	-0.12		0.47	0.13
	0.55	25.6	-0.22		0.58	0.22
7.1	0.55	21.0	-0.12		0.72	0.38
	0.57	8.9	-0.05		1.48	1.10
12.9	0.55			0.42	0.28	
244	0.45			0.30	0.26	

The spectra in the antiferromagnetic region could not be satisfactorily fitted with just one sextet component as noted previously [3–5]. It was possible to get reasonably satisfactory fits with two components as shown in figure 2 provided that the linewidth

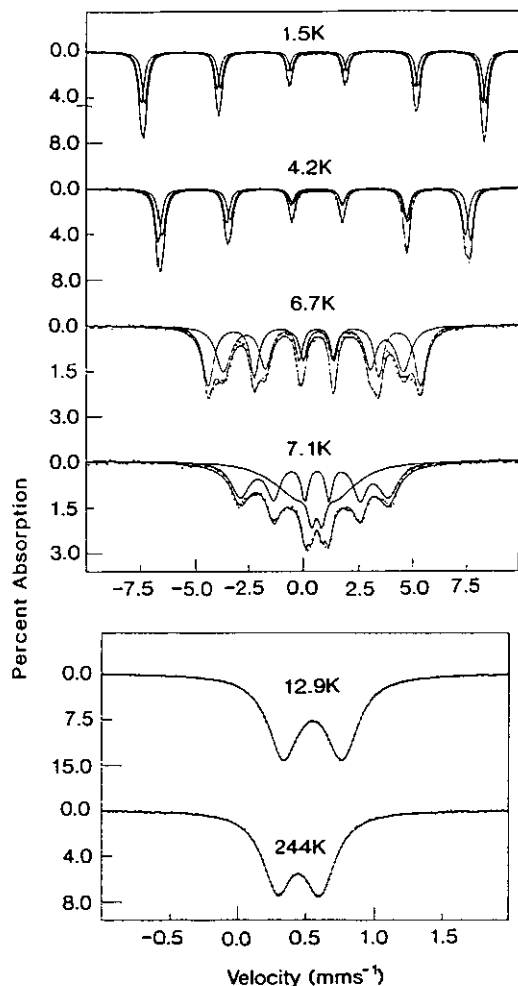


Figure 2. Powder spectra at various temperatures.

was allowed to become large just below the ordering temperature. Preliminary fits with two components showed very nearly the same absorption area for each and the final fits were made on the basis of equal area. The data also suggest the possibility of two closely spaced ordering temperatures (defined here as where B reaches zero) at approximately 7.15 K and 7.40 K, a difference in temperature slightly smaller than the 0.38 K difference in the reported [2] heat capacity anomalies. We are not certain of the existence of or reason for two ordering temperatures but if they are associated with the two heat capacity anomalies then the approximate equality of the entropy changes indicated in the heat capacity graphs [2] would simply connect with the approximately equal absorption strengths of the two Mössbauer components. We return to further discussion of the number of components and the line broadening in section 3.3.

3.2. Single-crystal spectra

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

and so we concentrate here on the further information which can be derived from the relative strengths of the absorption lines in the single-crystal spectra.

3.2.1. Spectra in the paramagnetic region. Some spectra taken with all three crystal orientations are shown in figure 3.

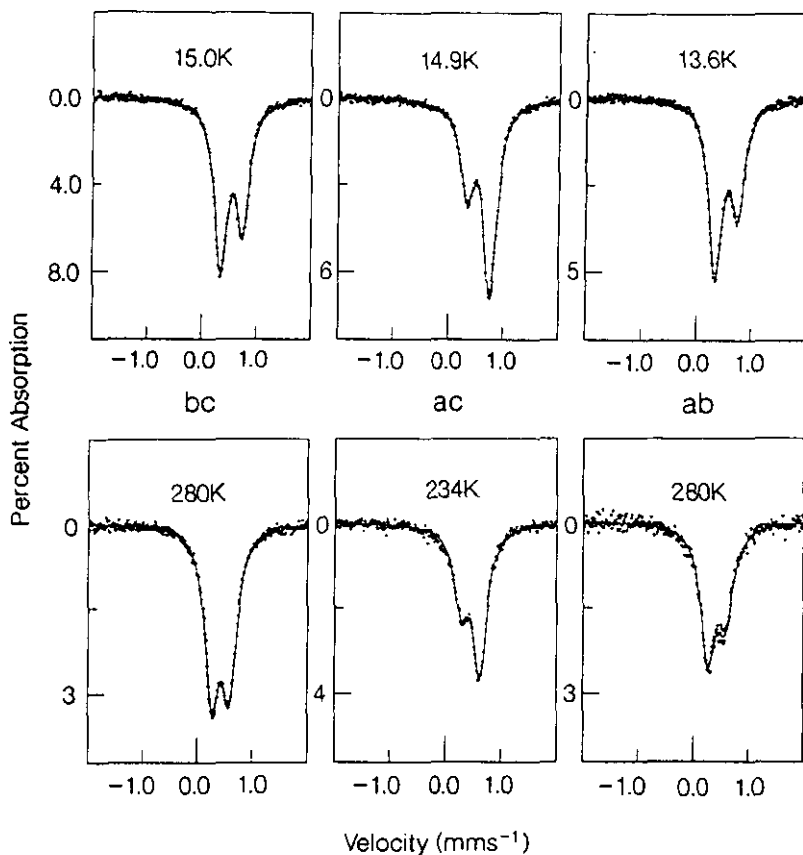


Figure 3. Some single-crystal spectra in the paramagnetic region. Here *ab*, for example, denotes an *ab*-plane absorber i.e. γ -rays parallel to the crystal *c* axis.

In Mössbauer spectroscopy the principal-axis system (PAS) of the EFG tensor is conventionally chosen such that $V_{zz} \geq V_{yy} \geq V_{xx}$. In $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ it may be expected that the *z* axis is close to the Fe–O direction which is at 41° to the crystal *a* axis [2]. In analysing their powder spectra Partiti *et al* [3] followed Misra and Sharp [6] in taking the *x* axis to be coincident with the crystal *b* axis. However, the work of Misra and Sharp [6] was an EPR study and furthermore the assignment of axes there is one [7] in which the splittings are ranked in the order *z*, *x*, *y*. We have also taken as a starting point, as seems likely from the structure, that the *b* axis is one of the EFG principal axes although not necessarily the *x* axis. The *ac*-plane absorber data was used to determine the asymmetry parameter η ; the data from the *bc*-plane absorber was then used to determine the orientations of the other two axes in the

ac plane. Data from the third (ab -plane) absorber was taken at a few temperatures as a check on the angles so deduced and consistency was found to within a few degrees. In this way we found V_{zz} to be negative, the crystal b axis to be the y axis of the EFG PAS, the angle between the z axis and the a axis to be approximately 50° at low temperature with perhaps a very small increase with temperature, and η to be approximately 0.6 at low temperature and decreasing significantly with increasing temperature.

Our results indicate that the z axis is not quite along the O-Fe-Cl(3) direction but at an angle to it of approximately 9° . This is probably due to the asymmetry in position of the Cl(2) and Cl(4) about the O-Fe-Cl(3) direction and a difference in the bonding of Cl(2) and Cl(4) [8]; it is possibly also an effect of the NH_4^+ ion. The origin of the temperature dependence of η is probably the same as that suggested [3] to explain the temperature dependence of the quadrupole splitting. Parameters of the electrostatic interaction are plotted in figure 4.

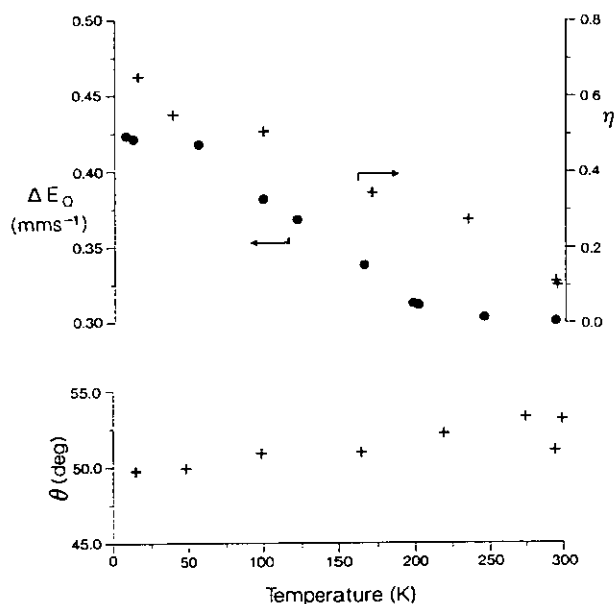


Figure 4. Temperature dependence of the electrostatic interaction. θ is the angle between the z and a axes.

3.2.2. Spectra in the antiferromagnetic region. Spectra taken at temperatures around 4.5 K for three crystal orientations are shown in figure 5. The almost total absence of 2,5 line intensity for the bc -plane absorber is striking, indicating that the hyperfine field is parallel or very nearly parallel to the a axis. The approximately 3:4:1 absorption ratios for the other two absorbers confirms this. We conclude unequivocally that the Fe spins are aligned along or very close to the a axis and not, as had previously been suggested [2], canted at an angle of approximately 40° to this axis.

More quantitatively, we fitted the spectra with a model similar to that of Kündig [9] in which line positions and intensities are computed as a function of the electric and magnetic hyperfine interaction parameters, the angular orientation of the magnetic field in the EFG PAS, and the direction of the γ -rays. The electrostatic parameters were taken to be those evaluated just above T_N as described in the

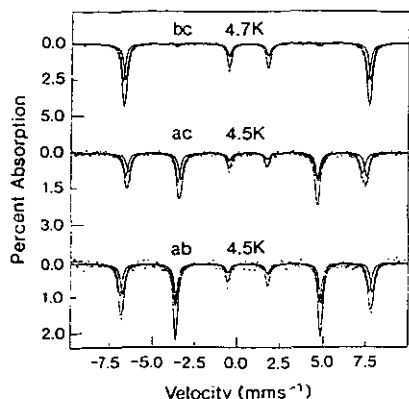


Figure 5. Single-crystal spectra in the antiferromagnetic region.

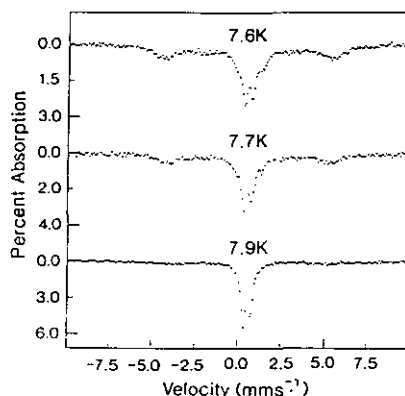


Figure 6. Spectra from a *bc*-plane absorber near the ordering temperature

previous section. Again we used two-component fits and examples of these are also shown in figure 5. The magnetic hyperfine fields were found to be within a few degrees of the *a* axis.

We note that, although our data show the spins to be aligned close to the *a* axis, they do not rule out some *small* canting of the spins. This might possibly be responsible for the magnetic susceptibility data of McElearney and Merchant [2] which are not characteristic of a pure antiferromagnet. We do not comment on this further at this stage except to report that we also measured susceptibilities of our own crystals and found similar behaviour.

Spectra taken with the *bc*-plane absorber close to the ordering temperature are shown in figure 6. Now if, according to the suggestion [2] that the lower-temperature heat capacity anomaly might be due to a spin reorientation approximately 0.4 K below the one ordering temperature, then the 2,5 line intensity would change from zero to being the strongest as the ordering temperature is approached from below. Although at these temperatures the lines are of course broadened, the 1,6 lines are still clear and there is evidently negligible 2,5 line absorption within approximately 0.2 K of the appearance of the purely doublet spectrum, contrary to the spin rotation suggestion. It may also be noted from figure 6 that ordering occurs at a temperature slightly higher (by approximately 0.5 K) than in the powder samples. This was also observed in other single-crystal samples and we suggest that this is due to stress in the crystal at low temperature arising from the setting in epoxy. A similar effect has been noted before [10].

3.3. Spectra near the ordering temperature

As already noted, the magnetically split spectra show considerable line broadening near the ordering temperature. To investigate this further we reanalysed the powder spectra (whose counting statistics are generally better than the single-crystal spectra) in two ways.

Firstly a distribution $P(B)$ of hyperfine fields was folded into a Kündig [9] type of spectrum computation where again the parameters of the electrostatic interaction were as deduced in section 3.2.1 and the experimental linewidth was fixed at 0.28 mm s^{-1} . Examples of fits are shown in figure 7 together with the

corresponding $P(B)$. The distributions especially around 6.5 K suggest clustering around discrete values of B . This suggested that a better basis might be a small number of components with broadening due to relaxation. Relaxation due to critical fluctuations near the ordering temperature is well known and in particular the spectra of a similar compound $\text{Cs}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ have been analysed this way by Chadwick *et al* [11], using a relaxation model based on the theory of Blume [12].

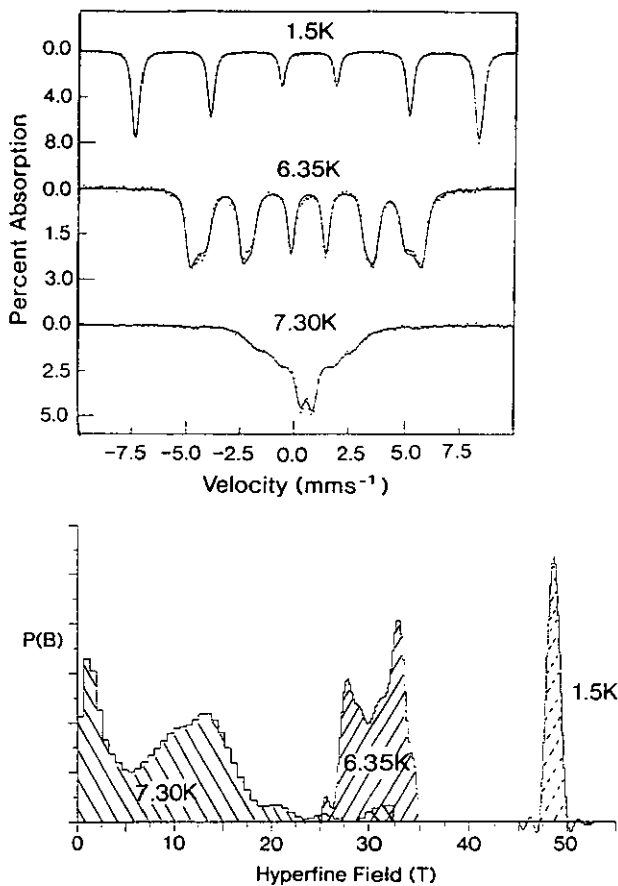


Figure 7. $P(B)$ fits at three temperatures and corresponding distributions. For display purposes the three vertical scales for $P(B)$ are different.

Examples of relaxation fits with two equal-absorption components are shown in figure 8. These are not perfect but, bearing in mind the approximations in the relaxation modelling, the main features of the spectra are reproduced rather well. We nevertheless also tried fitting with four components and these fits are shown also in figure 8; these are inevitably better and would not be sensibly improved with yet more components. The temperature dependence of the reduced magnetization deduced from our relaxation fits is shown in figure 9 together with fitted curves based on the critical behaviour expression given by Keller and Savic [13], parameters being fixed appropriate to a three-dimensional Heisenberg magnetic system. Overall we conclude that relaxation broadening due to critical fluctuations may explain our data satisfactorily. The fitted values of T_N for the two-component fits are 7.13 K and 7.36 K. Notably, the four-component fits give for all practical purposes the same two values of T_N .

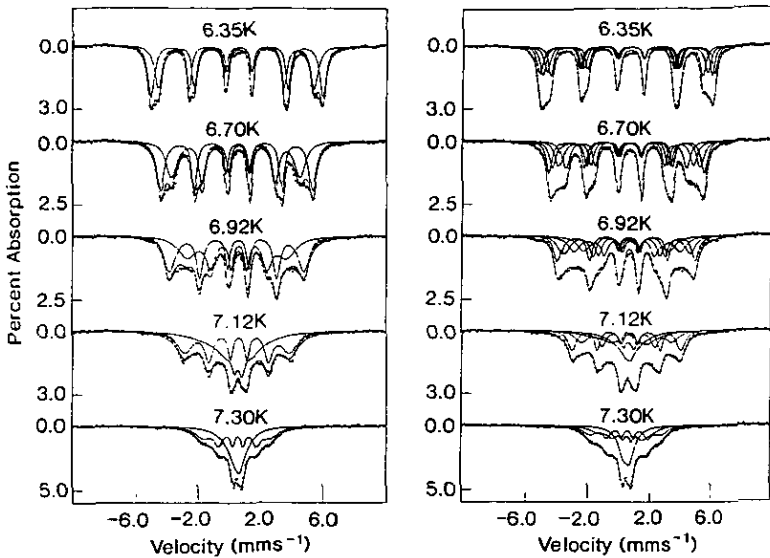


Figure 8. Relaxation fits with two and four components.

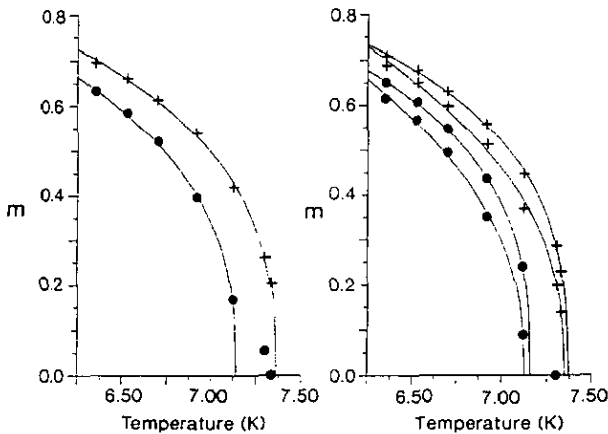


Figure 9. Temperature dependence of the magnetization parameter m of the relaxation model: two- and four-component fits.

We have shown that, with a physically realistic mechanism of line broadening, the spectra may be satisfactorily reproduced with four discrete components. It is possible although unlikely that two components would be sufficient with a different relaxation model giving somewhat different line shapes. However, the question remains: why more than one component? There are four iron sites in the unit cell and, as pointed out by Misra and Sharp [6], these are magnetically equivalent if a magnetic field lies in the ab or ac plane. Presumably, therefore, an exchange field in some other direction may result in more than one observed hyperfine field. But we have shown here that the Fe spins lie along the a axis, ruling out this possible explanation. Recently Calage *et al* [14] observed two clearly resolved components in $\beta\text{-(NH}_4)_2\text{FeF}_5$ and suggested that this was due to different orientations of the NH_4^+ ion giving different superexchange pathways. It seems likely that this effect also arises in $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ with perhaps some additional fracturing of the hyperfine field

resulting from small canting of the Fe spins from the a axis.

4. Conclusions

We have measured the Mössbauer spectra of $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ at many temperatures over the range 1.5 K to room temperature with powder and various single-crystal absorbers. In the paramagnetic region the sharply defined doublet spectra are well fitted with one component and we have deduced the parameters of the electric quadrupole hyperfine interaction. In the antiferromagnetic region the spectra required more than one component. The broadening of the spectra near the magnetic ordering temperature could be satisfactorily explained by relaxation effects due to critical fluctuations. On this basis the number of components required was found probably to be four and possibly only two; either way the fits indicated two ordering temperatures. Reasons for the number of components have been suggested. We have shown that in the antiferromagnetic phase the Fe spins are aligned close to the crystal a axis and not, as had previously been suggested, at a considerable angle to this axis. We found no evidence of a reported structural phase change in this compound just above the ordering temperature.

$(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ remains an interesting compound and merits further work. Applied-field experiments are under way and will be reported later.

Acknowledgments

We are grateful to Dr M P Brown for assistance with the X-ray measurements, and to Dr K O'Grady and Dr D P E Dickson for assistance with the susceptibility measurements. SRB acknowledges the support of an SERC studentship.

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