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Citation: AIP Conference Proceedings **5**, 436 (1972); doi: 10.1063/1.3699474
View online: https://doi.org/10.1063/1.3699474
View Table of Contents: http://aip.scitation.org/toc/apc/5/1
Published by the American Institute of Physics

MAGNETIC ORDERING IN A LINEAR CHAIN COMPOUND $RbFeCl_3$

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ABSTRACT

Results of neutron diffraction and Mössbauer effect studies of the hexagonal linear chain compound $RbFeCl_3$ are reported for the temperature range 1.2°K to room temperature. Three-dimensional magnetic ordering is found to occur at $T_N = 2.55 \pm .05$°K. Single crystal neutron scattering results above T_N are indicative of one-dimensional ferromagnetic correlations along the c-axis chains. Below T_N the magnetic moments μ are coupled ferromagnetically along the chains but lie in the basal plane, where they form an antiferromagnetic array. The hyperfine magnetic field H_{in} also lies in the basal plane and is nearly proportional in magnitude to μ. The temperature dependence of H_{in} and μ indicates a 0°K saturation value for μ of about 2 μ_β.

Properties characteristic of one-dimensional magnetic ordering are to be expected in $RbFeCl_3$ on the basis of its structure: the Fe^{2+} ions are arranged in linear chains with an interchain separation (7Å) more than double the intrachain separation (3Å).[1,2] Magnetic susceptibility measurements have been interpreted in terms of ordering into linear antiferromagnetic chains.[2] We report here the results of neutron diffraction and Mössbauer effect studies undertaken to clarify the nature of the magnetic ordering and Fe^{2+} bonding.

$RbFeCl_3$ belongs to the hexagonal space group $P6_3/mmc(D^4{}_{6h})$.[1] The chains lie along the c-axis and consist of slightly distorted $(FeCl_6)^{4-}$ octahedra which share their {111} faces. The Fe^{2+} site symmetry is trigonal (D_{3d}).

The material was prepared by careful dehydration and reduction of a solution of Rb_2CO_3 and Fe_2O_3 in dilute HCl.[3] Single crystals 0.5 to 1 cc in volume were grown by the Bridgman technique. The crystals had (100) cleavage planes.

Powder neutron diffraction data at 4.2°K were consistent with the room temperature space group. The lattice constants at 4.2°K were $a_o = 6.99$ Å and $c_o = 5.95$ Å. There were no signs of magnetic order. However, a small additional low-angle peak was observed at 1.6°K. Data taken on a single crystal at 4.2°K and 1.86°K confirmed the existence at 1.86°K of a set of $(h/3, h/3, \ell)$ magnetic reflections with $h \neq 3n$ and $\ell = 2n$. (These and all following indices are based on the chemical unit cell). The first condition is characteristic of the triangular structure observed in other

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*Work supported by U.S. Atomic Energy Commission.

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compounds of this type,[4,5] but the second corresponds to ferromagnetic coupling along the chains rather than the antiferromagnetic coupling seen in the isostructural $RbNiCl_3$ and $CsNiCl_3$.[4,5]

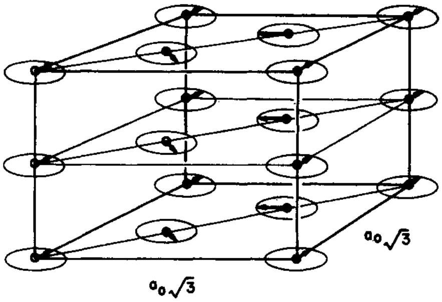

Fig. 1 Magnetic unit cell of $RbFeCl_3$ (not to scale).

Comparison of observed and calculated intensities gave a good fit (Table I) for a structure of the type shown in Fig. 1. The volume of the magnetic unit cell is three times that of the chemical unit cell, and the a-axis of the magnetic cell makes an angle of 30° with the a-axis of the chemical cell. The moments lie in the basal plane, with adjacent moments in the plane directed 120° apart to form an antiferromagnetic array. The actual orientation of this array with respect to the [100] axis cannot be determined by neutron diffraction.

The magnitude of the Fe^{2+} moment at 1.86°K was found to be $1.6 \pm 0.2\ \mu_\beta$. The uncertainty is due to the limited amount of nuclear data collected and the difficulty of making proper correction for extinction effects. A check on this result is provided by the value derived from the (1/3 1/3 0) powder peak: $2.0 \pm 0.2\ \mu_\beta$ at 1.6°K.

The variation of the magnetic moment with temperature was determined by following the intensity of the single crystal (1/3 1/3 0) peak and is displayed in Fig. 2. The intensity of the critical scattering close to this Bragg reflection had a maximum at $2.55 \pm .05$°K, which was taken to be the Neel point (T_N).

The nature of the critical scattering above T_N was also studied. There is marked three-dimensional character at 4.2°K, and even some as high as 10°K, but at 20°K the scattering takes the form of reciprocal lattice planes perpendicular to the c-axis at $\ell = 2n$, indicative of one-dimensional ferromagnetic correlations along the c-axis. Some of these data are shown in Fig. 3. Unfortunately, the peak-to-background ratio was poor, and scans across the planes gave broad peaks. The correlation length at 20°K is approximately 3 Å, about one-seventh the value found in $(CD_3)_4NMnCl_3$(TMMC).[6] Although there appeared to be a 20% decrease in this length at 50°K, the change was barely outside counting statistics.

Table I. Observed and calculated intensities for single crystal $RbFeCl_3$ at 1.86°K. I_{calc} is based on an Fe^{2+} moment of $1.6\ \mu_\beta$.

hkl	I_{calc}	I_{obs}
1/3 1/3 0	201	200
2/3 2/3 0	88	80
1/3 1/3 2	63	67
4/3 4/2 0	27	28

The Fe^{57} Mössbauer absorption spectra were taken using a

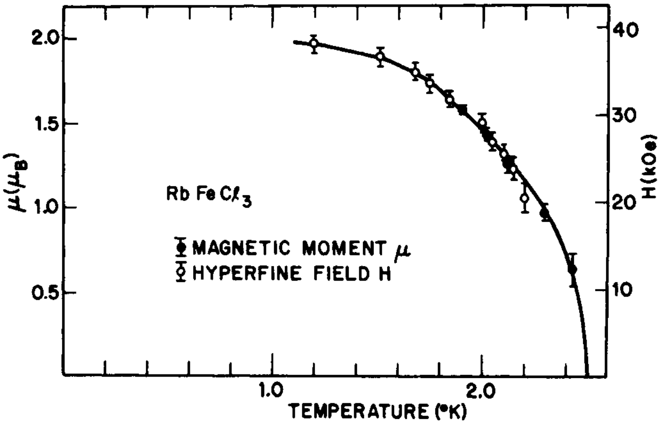

Fig. 2 Temperature dependence of magnetic moment and hyperfine field.

constant acceleration spectrometer and a Co^{57} in Pd source.

Spectra at 4.2°K and above show no hyperfine splitting, despite the observed spin correlations. Hyperfine parameters obtained at selected temperatures in the paramagnetic region are summarized in Table II. The negative sign of the quadrupole splitting (Q.S.) was inferred from the asymmetry of the peak intensities observed using an absorber made up of a mosaic of (100) single crystal platelets.[7] This sign is consistent with that required to fit data below T_N. Since the Fe^{2+} ion is at a site of D_{3d} symmetry, the negative sign implies that the ground state wavefunction is predominantly of

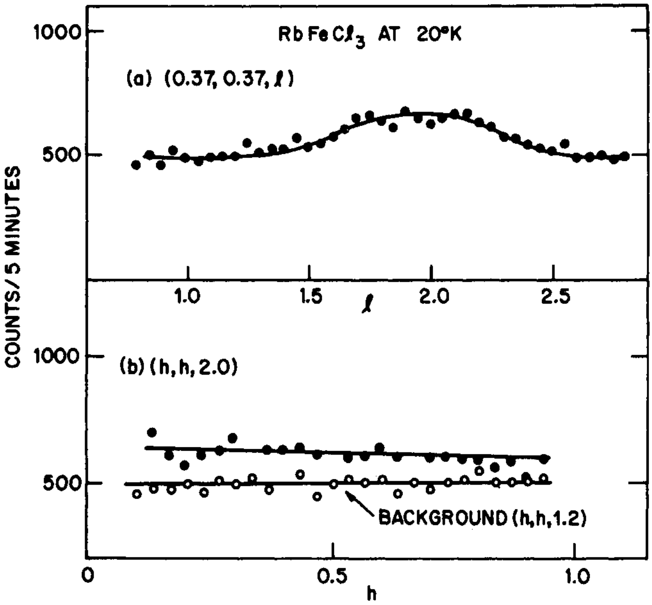

Fig. 3 Neutron diffraction data from $RbFeCl_3$ single crystal at 20°K. (a) scan along (0.37, 0.37, ℓ), perpendicular to reciprocal lattice plane; (b) scan in a plane along (h, h, 2.0) direction and background scan.

Table II. Hyperfine parameters above T_N.

T ($^\circ$K)	Q.S.[a] (mm/sec)	I.S[b] (mm/sec)
296	$-1.49\pm.01$	$1.08\pm.01$
78	$-1.80\pm.01$	$1.22\pm.01$
4.2	$-1.87\pm.01$	$1.23\pm.01$

[a] Q.S. = quadrupole splitting $e^2qQ/2$; $\eta = 0$ by symmetry.

[b] I.S. = isomer shift relative to iron foil at 296° K.

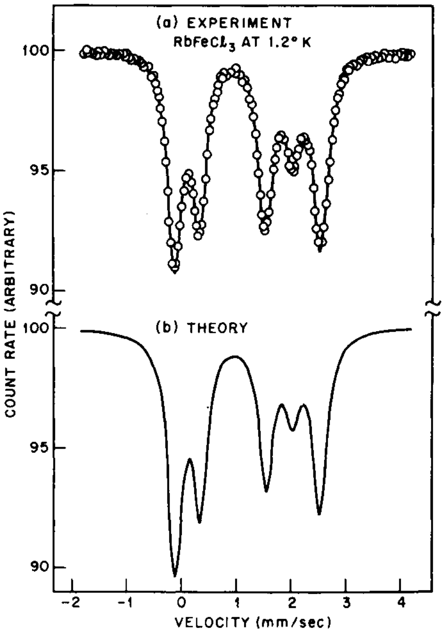

Fig. 4 Mössbauer spectrum at 1.2°K. (a) measured; (b) calculated for H = 38 kOe, $e^2qQ/2 = -1.87$ mm/sec, $\eta = 0$, and $\theta = 90^\circ$.

orbital singlet character (Y_2^0),[8] in agreement with an analysis of the magnetic susceptibility data.[2]

The magnitudes of Q.S. and the isomer shift (I.S.) are indicative of covalency in the Fe^{2+} bonding. The room temperature I.S. corresponds to a $3d^6 4s^{0.2}$ configuration according to the I.S. calibration of Danon.[9] Comparison of the 4.2°K Q.S. with splittings observed in other trigonally distorted octahedral compounds[10] yields a radial parameter $\langle r^{-3}\rangle_{3d} \approx 2$ a.u., indicative of substantial d-electron delocalization with respect to the free ion ($\langle r^{-3}\rangle_{3d} = 5.1$ a.u.).

Spectra below T_N are magnetically split into an apparent doublet and an apparent triplet, a result characteristic of a small hyperfine field directed perpendicular to the electric field gradient (EFG) principal axis.[11] Good fits to the 1.2°K spectrum (Fig. 4) were obtained with hyperfine field $H_{in} = 38\pm1$ kOe, Q.S. parameter $e^2qQ/2 = -1.87\pm.01$ mm/sec, and asymmetry parameter $\eta = 0.1\pm0.1$. The polar angle of H_{in} in the EFG principal axis system was $\theta = 90\pm10^\circ$. The quality of the fit was insensitive to the azimuthal angle φ. Since $e^2qQ/2$ is not altered by the magnetic transition, the direction of the principal axis below T_N must be nearly parallel to the c-axis, the direction required by symmetry above T_N. Thus, our value for θ indicates that H_{in} is directed approximately perpendicular to the c-axis, as are the magnetic moments.

With the above hyperfine parameters, the Fe^{57} ground state magnetic splitting is very nearly equal to the doublet splitting. Values of H_{in} determined from the doublet splitting are plotted against temperature T in Fig. 2, along with the magnetic moment data. The vertical scales are chosen to match the two data sets at 1.9°K. The plot indicates that the two quantities are nearly proportional and suggests that the moment μ will saturate at a rather low value, about 2.0 μ_β.

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