PHYSICAL REVIEW B VOLUME 31, NUMBER 5 1 MARCH 1985

Linear-chain antiferromagnetism in $FeOHSO_4$ and $FeOHCrO_4$

M. G. Townsend*
Laboratoire de Crystallographie, Centre National de la Recherche Scientifique, Grenoble, France

G. Longworth
Atomic Energy Research Establishment, Harwell, England

J. E. Dutrizac
Department of Energy, Mines and Resources, Ottawa, Canada K1A 0G1

(Received 14 August 1984)

$FeOHSO_4$ and $FeOHCrO_4$ order magnetically in three-dimensional magnetic lattices at about 111 K and at 104.0±0.5 K, respectively, as determined by Mössbauer spectroscopy and neutron diffraction. Magnetic susceptibility and neutron-diffraction data show that above these temperatures these materials are linear-chain, Heisenberg antiferromagnets. The intrachain (J_1) and interchain magnetic-exchange interactions in $FeOHSO_4$ are determined to be -19 K and $|4|$ K, respectively, by fitting magnetic susceptibility data to a linear-chain model and applying Oguchi's method. A similar analysis for $FeOHCrO_4$ yields $J_1=-32$ K and an interchain interaction of $|3|$ K. The magnetic structure of $FeOHCrO_4$, determined from neutron diffraction, is compared to that of $FeOHSO_4$ by using the Fourier method of Bertaut.

INTRODUCTION

In orthorhombic basic iron sulfate, $FeOHSO_4$, x-ray diffraction studies of single crystals have shown that the Fe^{3+} cations are octahedrally coordinated by two hydroxyl groups and four sulfate oxygens. These cations are in infinite linear chains and are joined by single OH bridges making an angle of about 20° with the linear chain. The distance between Fe^{3+} cations along the chain is about 3.65 Å. The shortest distance between Fe^{3+} cations belonging to neighboring chains is 5.13 Å.[1] However, as shown in this work, interchain magnetic exchange interactions occur primarily between Fe^{3+} cations 6.35 Å apart and these are connected through a sulfate group.

Scheerlinck and Legrand demonstrated from neutron-diffraction studies that the spins of Fe^{3+} cations in $FeOHSO_4$ were coupled antiferromagnetically along the chain direction (a axis),[2] confirming the speculation of Rumbold and Wilson[3] based on their Mössbauer and magnetic susceptibility results.

Mössbauer magnetic hyperfine spectra of $FeOHSO_4$ recorded by Rumbold and Wilson persisted up to ≃90 K.[3] This was interpreted in terms of intrachain spin correlation with relaxation effects caused by interchain spin relaxation. In contrast, neutron-diffraction data of Scheerlinck and Legrand[2] together with Mössbauer data of this work show that three-dimensional magnetic ordering exists up to about 111 K.

The structure of $FeOHCrO_4$ has not been determined, but x-ray powder diffraction shows a monoclinic cell.[4] This monoclinic supercell results from a small distortion of the orthorhombic cell. In the present work, powder-neutron-diffraction and magnetic susceptibility results suggest the presence of infinite chains of Fe^{3+} cations similar to those in $Fe(OH)SO_4$. All neutron magnetic reflections in $FeOHCrO_4$ can be indexed either in a monoclinic or in an orthorhombic cell. $FeOHCrO_4$ was reported to be ferromagnetic below 71 K;[5] the present results show, however, that the material is antiferromagnetic at temperatures below 104±0.5 K.

EXPERIMENTAL AND RESULTS

The basic iron sulfate, $FeOHSO_4$, was formed by reacting 650 g of $Fe_2(SO_4)_3\cdot 6H_2O$ with 350 g of H_2O at 190 °C in a glass-lined titanium autoclave. The charge was heated for 5 h while stirring at 600 rpm. The product was then rapidly cooled, and filtered and washed with a small amount of cold water and then with methanol. If large

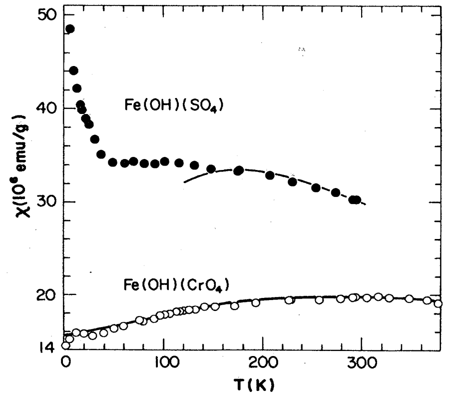

FIG. 1. Magnetic susceptibilities at various temperature for $FeOHSO_4$ and $FeOHCrO_4$ with fits to experimental data using a Bonner-Fisher, linear-chain model (Refs. 8 and 9).

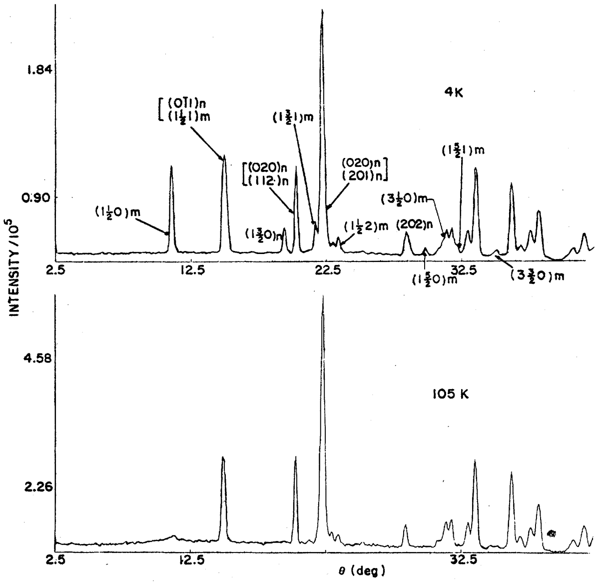

FIG. 2. Neutron-diffraction patterns of $FeOHCrO_4$ at 4 and 105 K. The lines are indexed for an orthorhombic cell: $a = 7.50$ Å, $b = 6.68$ Å, $c = 7.26$ Å at 4 K.

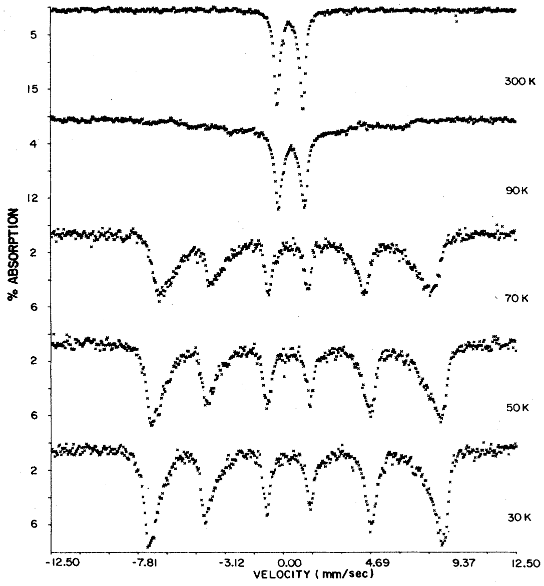

FIG. 3. Mössbauer spectra of $FeOHSO_4$ at various temperatures.

amounts of water were employed for the washing, the product developed an orange tinge, indicating the formation of an amorphous impurity phase. The methanol was removed under vacuum at 25 °C and the product was finally dried at 110 °C. The product was pale yellow in color and was shown by x-ray diffraction to consist only of $FeOHSO_4$. The chemical analysis of the product is given below and it is evident that the real product is slightly iron deficient and SO_4-rich. Since OH was determined by difference only, its determination is not overly accurate.

	Current synthesis	$FeOHSO_4$
Fe	31.93%	33.06%
SO_4	57.37%	56.87%
OH	10.70%	10.06%

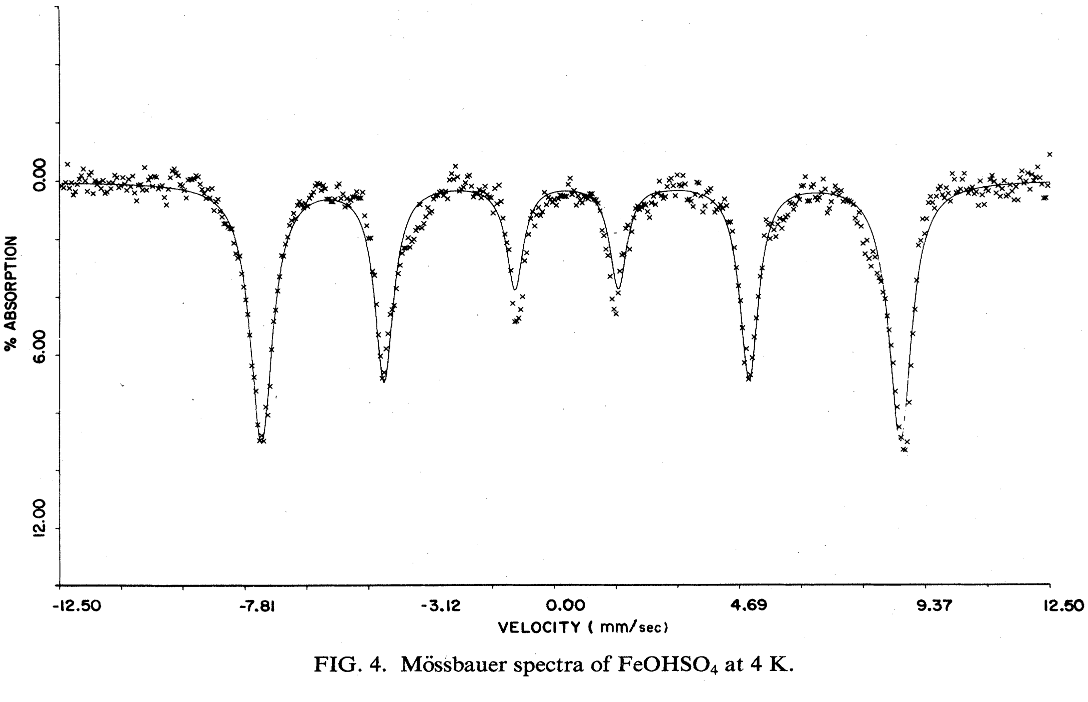

FIG. 4. Mössbauer spectra of $FeOHSO_4$ at 4 K.

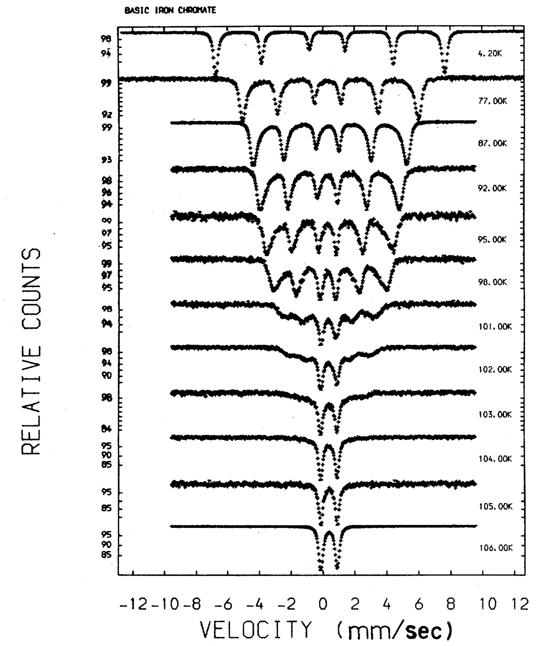

FIG. 5. Mössbauer spectra of $FeOHCrO_4$ at various temperatures.

The basis iron chromate was synthesized by reacting one liter of 1.0 M $Fe(NO_3)_3$ with 2.0 M CrO_3 in a solution whose pH was adjusted to 0.5 by HNO_3/Li_2CO_3 additions. The charge was heated for 24 h at 175 °C in an autoclave using a 600 rpm stirring speed. The product which was reddish purple was rapidly cooled to room temperature, filtered and washed with H_2O, and subsequently dried at 110 °C. The use of a concentrated acidic medium at high temperature was necessary to avoid the production of amorphous iron chromates. X-ray diffraction analysis indicated the presence of only $FeOHCrO_4$ and chemical analysis yielded a product containing near-stoichiometric CrO_4 but slightly deficient in iron (and enriched in $\bar{OH}$ since this is determined by difference).

	Current synthesis	$FeOHCrO_4$
Fe	28.27%	29.57%
CrO_4	61.54%	61.42%
OH	10.19%	9.00%

Both the basic iron chromate and basic iron sulfate powders were stable in air and were stored in a desiccator to exclude adsorption of surface moisture.

Magnetic susceptibilities of powdered $FeOHSO_4$ and $FeOHCrO_4$ were recorded with a commercial vibrating sample magnetometer and associated cryostat at temperatures between 2 and 380 K. The equipment and method of measurement have been described elsewhere.[6] The results are shown in Fig. 1. A detailed comparison of the susceptibilities with data previously reported is planned to be published.[7] Fits to the experimental curves with a linear-chain model[8,9] for $Fe(OH)SO_4$ and for $FeOHCrO_4$ are shown. There is a weak paramagnetic component at low temperature in $FeOHSO_4$ which probably arises from a small second phase in our specimen and here we have fitted only the higher-temperature data.

Neutron diffraction was carried out on the multidetector powder diffractometer DlB at Institute Laue-Langevin, Grenoble. The powder patterns for $FeOHCrO_4$

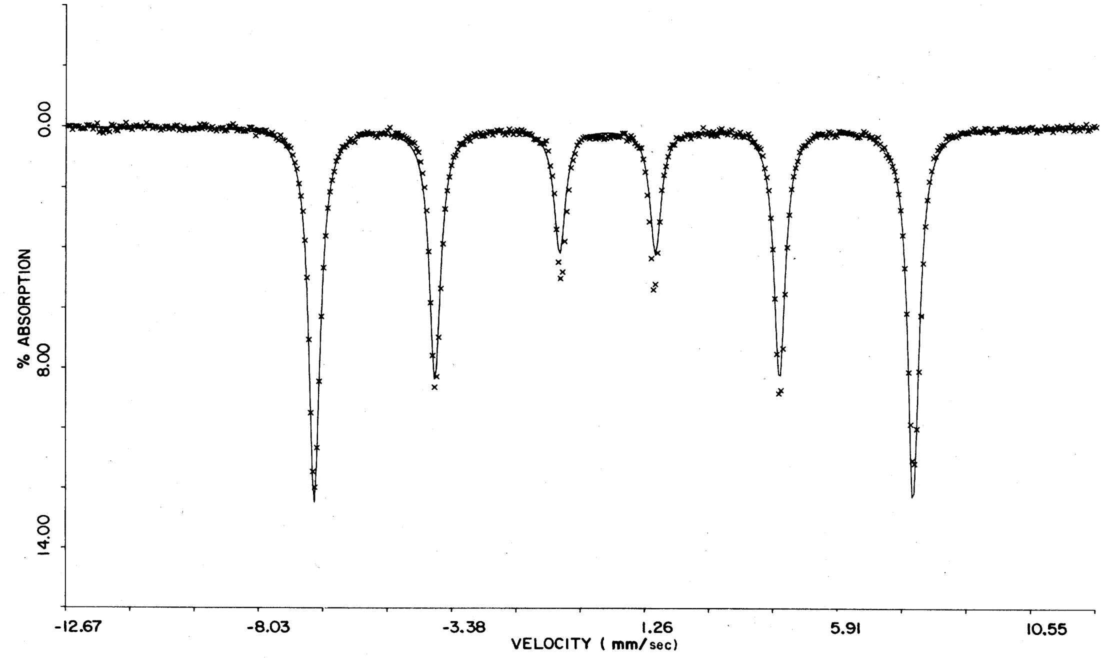

FIG. 6. Mössbauer spectrum of $FeOHCrO_4$ at 4 K.

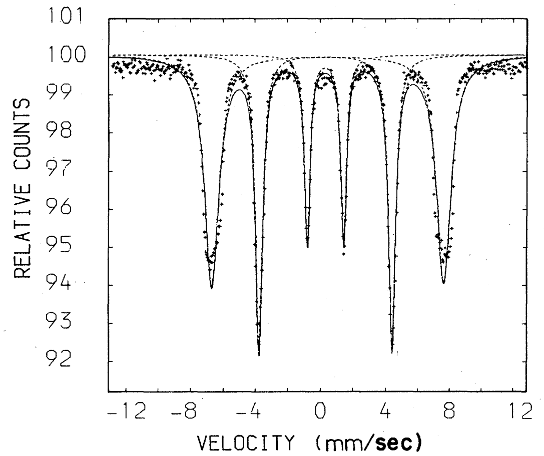

FIG. 7. Mössbauer spectrum of $FeOHCrO_4$ at 4 K in an external field of 40 kOe.

at 4 and 105 K are shown in Fig. 2. $FeOHCrO_4$ is monoclinic[2] ($a=13.28$ Å, $b=7.23$ Å, $c=13.12$ Å, $\beta=121.3°$ at 4 K) but for comparison with orthorhombic $FeOHSO_4$ all the magnetic reflections can also be indexed in an orthorhombic cell ($a=7.50$ Å, $b=6.68$ Å, and $c=7.26$ Å). This cell is slightly larger than the orthorhombic cell of $FeOHSO_4$ ($a=7.28$ Å, $b=6.33$ Å, and $c=7.10$ Å at 4 K).[5]

Fe atoms are in special positions in the orthorhombic cell ($Pnma$) and the positions (x_2,y_2,z_2) in the monoclinic cell ($P2_{1/c}$) can be related to those in the orthorhombic cell (x_1,y_1,z_1) by a matrix:

$$\begin{vmatrix} x_2 \\ y_2 \\ z_2 \end{vmatrix} = \begin{vmatrix} x_1 \\ y_1 \\ z_1 \end{vmatrix} \begin{vmatrix} \frac{1}{3} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \\ \frac{2}{3} & 0 & 0 \end{vmatrix} .$$

The indices of the magnetic reflections are related by the inverse transposed matrix in standard fashion.[10] Similarly, x-ray reflections for $FeOHCrO_4$, indexed in a monoclinic cell,[11(a)] may be related to corresponding x-ray reflections for $FeOHSO_4$ indexed in orthorhombic symmetry.[11(b)]

Mössbauer spectra of $FeOHSO_4$ and $FeOHCrO_4$ were recorded on a conventional spectrometer with a constant-acceleration drive at temperatures between 4 and 300 K. Spectra were computer fitted by a least-squares iterative procedure.[12] Spectra of $FeOHSO_4$ at various temperatures are shown in Figs. 3 and 4. The parameters of the $FeOHSO_4$ spectrum at 10 K are H, the internal field equal to 510 kOe; θ, the polar angle of internal field in the principal axes of the electric-field gradient, equal to 40°; η, the asymmetry parameter, equal to 0.0; $\frac{1}{2}e^2qQ$, the quadrupole interaction, equal to 0.78 mm/sec, S_I, the isomer shift, equal to 0.54 with respect to Fe; linewidth equal to 0.5 mm/sec; and a dimensionless hyperfine field distribution parameter[12] of 0.02. The spectra of $FeOHCrO_4$ at various temperatures and at 4 K in an external field of 40 kOe are shown in Figs. 5—7. The parameters for the $FeOHCrO_4$ spectrum at 4 K in zero-applied field are $H=439$ kOe, $\theta=42°$, $\eta=0.0$, $\frac{1}{2}e^2qQ=0.51$, $S_I=0.49$ and linewidth equal to 0.28 mm/sec.

Plots of the Mössbauer magnetic hyperfine field against temperature for $FeOHSO_4$ and $FeOHCrO_4$ are shown in

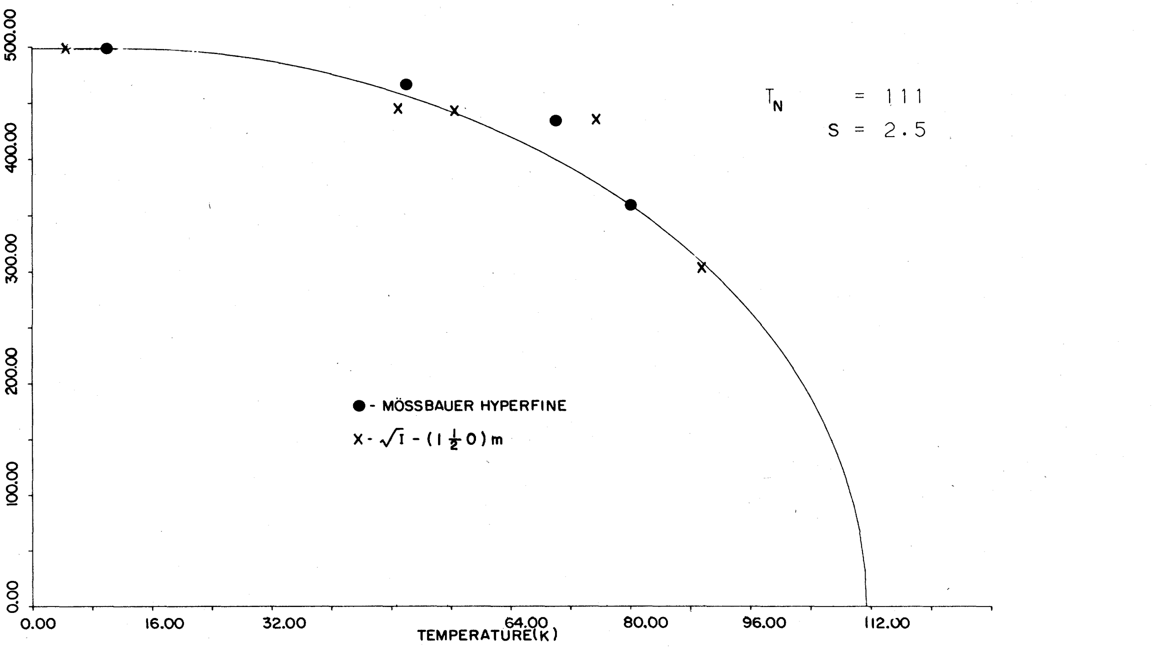

FIG. 8. Mössbauer magnetic hyperfine field (●) for $FeOHSO_4$ and (x) $-\sqrt{I}$ against temperature [where I is the intensity of the $(1,\frac{1}{2},0)$ magnetic reflection of $FeOHSO_4$ in an (a,b,c) cell taken from Scheerlinck (Ref. 2)].

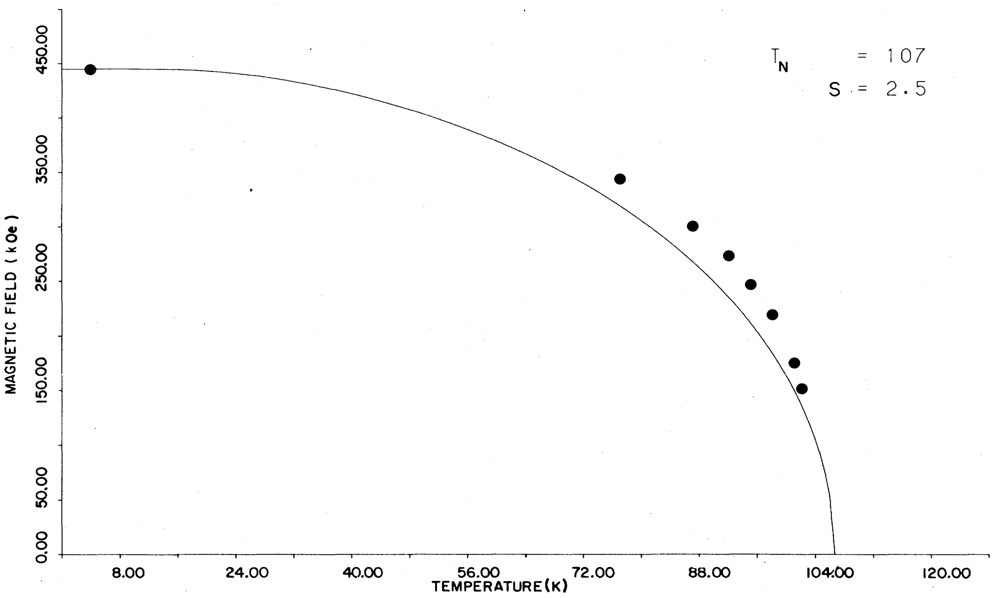

FIG. 9. Mössbauer magnetic hyperfine field of $FeOHCrO_4$ against temperature.

Figs. 8 and 9, respectively. Also indicated for $FeOHSO_4$ in Fig. 8 are the $\sqrt{I}$ (I equals intensity of the $(1,\frac{1}{2},0)$ magnetic reflection,[2] normalized to the hyperfine field data at 4 K. The data points have been fitted to magnetization curves derived from Brillouin functions with $S=\frac{5}{2}$ (for Fe^{3+}); extrapolation of these curves to 0 suggests three-dimensional magnetic ordering temperatures of 111 and 107 K for $FeOHSO_4$ and $FeOHCrO_4$, respectively. However, the Brillouin curve does not fit the experimental points well at temperatures just below T_N. Therefore, Mössbauer spectra for $FeOHCrO_4$, at one-degree intervals between 101 and 106 K, Fig. 5, were used to determine the ordering temperature to be 104.0±0.5 K. Near T_c, the reduced magnetization is expected to vary as $(T_c-T)^{\beta}$. For the few points within 10% of T_c, β is approximately 0.3, close to the value to be expected for three-dimensional ordering.[13]

DISCUSSION

Our neutron-diffraction data show that in orthorhombic symmetry, the b axis in $FeOHCrO_4$ is doubled in the magnetic cell. The magnetic structure is a simple collinear one with spins coupled antiferromagnetically along the chain direction (a axis in the orthorhombic system). The magnetic intensities fit with a spin direction (in the orthorhombic system, $a,b,c\equiv x,y,z$) of polar angle, $\theta\simeq30°$ and azimuthal angle, $\phi\simeq10°$.

Short-range magnetic order, indicated by a broad hump at low angle ($\theta\simeq10°$) of reflection is observed in $FeOHCrO_4$ at 105 K, Fig. 2, and this persists up to 140 K. The progressive broadening of the low-angle magnetic reflection with increasing temperature results from a diminishing correlation length between magnetic chains.[14] Such effects increase from three-dimensional through two-dimensional to one-dimensional systems.[12] A similar broad hump at low diffraction angle was observed in $FeOHSO_4$ at temperatures above T_N.[2]

Scheerlinck and Legrand[2] have applied the Fourier method of Bertaut[15] to the magnetic lattice of $FeOHSO_4$. This method is applicable to Heisenberg systems such as Fe^{3+} magnetic materials.[15] The Fourier transform in reciprocal space of the exchange interaction is minimized with respect to the reciprocal-lattice vectors (h,k,l) leading to the energies of various possible magnetic structures. Stability conditions are derived from the second derivative of the Fourier transform. The exchange integrals and their Fourier transforms applicable to $FeOHSO_4$ or $FeOHCrO_4$ are shown in Table I. Scheerlinck and Legrand[2] find three magnetic modes: the $(2\pi,2\pi,0)$ mode,

$$E=-2J_1-2J_3+2J_4+4J_6-4J_7\ , \tag{1}$$

the $(2\pi,2\pi,2\pi)$ mode,

$$E=-2J_2-2J_3-2J_4+4J_6+4J_7\ , \tag{2}$$

and the helical mode,

$$E=\frac{4J_1J_3J_4}{J_2^2}-2J_1-2J_3-2J_4\ . \tag{3}$$

Here, for example, for solution (1), values of (h,k,l) equal to $(2\pi,2\pi,0)$, respectively, are derived from the minimization process and are then substituted in the energy eigenvalue. The helical mode has the lowest energy (E) but the stability conditions are not fulfilled. The energies of modes (1) and (2) are equal when $J_4=2J_7$.

Above about 55 K the magnetic structure of $FeOHSO_4$ (Ref. 2) is similar to that which we have determined for $FeOHCrO_4$ at temperatures below 104 K, and both can be described by the $(2\pi,2\pi,0)$ mode. The spins are coupled antiferromagnetically along the a axis, and the b axis is doubled in the magnetic cell. The stability conditions are

TABLE I. Study of the Bertaut modes in (a,b,c) orthorhombic cell.

Exchange integral	Number of equivalent neighbors	Distance to Fe atom at (0,0,0)	Coordination in an (a,b,c) cell		Fourier transform $\sum_i J_i e^{i\mathbf{k}\cdot\mathbf{r}_i}$
J_1	2	3.63 Å	$(\frac{1}{2},0,0)$	$(-\frac{1}{2},0,0)$	$2\cos\left[\frac{h}{2}\right]J_1$
J_2	8	5.08 Å	$(\frac{1}{4},\frac{1}{2},\frac{1}{2})$	$(-\frac{1}{4},\frac{1}{2},\frac{1}{2})$	
			$(\frac{1}{4},-\frac{1}{2},\frac{1}{2})$	$(-\frac{1}{4},-\frac{1}{2},\frac{1}{2})$	$8\cos\left[\frac{h}{4}\right]\cos\left[\frac{k}{2}\right]\cos\left[\frac{l}{2}\right]J_2$
			$(\frac{1}{4},\frac{1}{2},-\frac{1}{2})$	$(-\frac{1}{4},\frac{1}{2},-\frac{1}{2})$	
			$(\frac{1}{4},-\frac{1}{2},-\frac{1}{2})$	$(-\frac{1}{4},-\frac{1}{2},-\frac{1}{2})$	
J_3	2	6.35 Å	$(0,1,0)$	$(0,-1,0)$	$2\cos(k)J_3$
J_4	2	7.06 Å	$(0,0,1)$	$(0,0,-1)$	$2\cos(l)J_4$
J_5	8	7.22 Å	$(\frac{3}{4},\frac{1}{2},\frac{1}{2})$	$(-\frac{3}{4},\frac{1}{2},\frac{1}{2})$	
			$(\frac{3}{4},-\frac{1}{2},\frac{1}{2})$	$(-\frac{3}{4},-\frac{1}{2},\frac{1}{2})$	$8\cos\left[\frac{3h}{4}\right]\cos\left[\frac{k}{2}\right]\cos\left[\frac{l}{2}\right]J_5$
			$(\frac{3}{4},\frac{1}{2},-\frac{1}{2})$	$(-\frac{3}{4},\frac{1}{2},-\frac{1}{2})$	
			$(\frac{3}{4},-\frac{1}{2},-\frac{1}{2})$	$(-\frac{3}{4},-\frac{1}{2},-\frac{1}{2})$	
J_6	4	7.31 Å	$(\frac{1}{2},1,0)$	$(-\frac{1}{2},1,0)$	$4\cos\left[\frac{h}{2}\right]\cos(k)J_6$
			$(-\frac{1}{2},1,0)$	$(-\frac{1}{2},-1,0)$	
J_7	4	7.94 Å	$(\frac{1}{2},0,1)$	$(-\frac{1}{2},0,1)$	$4\cos\left[\frac{h}{2}\right]\cos(l)J_7$
			$(\frac{1}{2},0,-1)$	$(-\frac{1}{2},0,-1)$	

$J_1<0$, and $J_1J_3-J_2^2>0$; also $2J_4-4J_7<0$, i.e., the energy of the $(2\pi,2\pi,0)$ mode is lower than that of the $(2\pi,2\pi,2\pi)$ mode.

In $FeOHSO_4$ at temperatures below 55 K, Scheerlinck and Legrand[5] reported an additional magnetic reflection $(1,\frac{1}{2},\frac{1}{2})$ in the orthorhombic (a,b,c) cell. This led them to deduce a coexistence of the $(2\pi,2\pi,0)$ and $(2\pi,2\pi,2\pi)$ modulations below 55 K. Thus they proposed a magnetic phase transition: Above 55 K, $J_4-2J_7<0$, while below 55 K, $J_4=2J_7$. They derived a noncollinear structure below 55 K by combining the two modulations at 90° out of phase, and fitting the direction of the resultant to the experimental intensities. Evidently, from our data, such a structure does not occur in $FeOHCrO_4$ where the $(2\pi,2\pi,0)$ mode is stable down to 0 K, i.e., $J_4<2J_7$ at temperatures below 104 K.

Scheerlinck and Legrand's[2] theoretical analysis is correct and their solution ingenious. However, from powder neutron diffraction alone, it would not be easy to distinguish their proposed coupling of two modulations from two separate magnetic phases coexisting in the same crystal structure, or from two coexisting magnetic chemical phases. They synthesized $FeOHSO_4$ by the method of Posjnak and Merwin;[16] the orange-yellow color of their product does suggest that more than one phase may be present. Rumbold and Wilson[3] also used Posjnak's[16] method of preparation. The temperature (56 K) at which they observed a peak in the magnetic susceptibility coincides approximately with the temperature below which Scheerlinck and Legrand believe they observe the $(2\pi,2\pi,2\pi)$ modulation.[2] The latter interpretation requires confirmation by a careful neutron-diffraction study of the phase diagram in this region.

The relatively flat magnetic susceptibility curves for $FeOHSO_4$ and $FeOHCrO_4$ and lack of Curie-law dependence in the higher temperature range, Fig. 1, show quite clearly the effects of one-dimensional magnetic correlations. It is, however, surprising that there is no apparent peak in the susceptibilities of $FeOHSO_4$ and $FeOHCrO_4$ at 111 and 104 K, respectively, indicating the onset of three-dimensional antiferromagnetic order.

Numerical calculations have been made for the susceptibility of a Heisenberg, linear chain for different values of S.[8,9] These calculations are based on the Bonner-Fisher method that calculates the thermodynamic and magnetic properties exactly for a sequence of small finite spin chains with steadily increasing chain length for both periodic and free-end boundary conditions. Extrapolations are then made to the thermodynamic limit. We can calculate the values of J_1, the magnetic-exchange interaction along the chain, by comparing the Bonner-Fisher theoretical calculations with the data. Fits to the linear-chain model, Fig. 1, yield $J_1=-19$ and -32 K, for $FeOHSO_4$ and $FeOHCrO_4$, respectively. In this fit there are only two adjustable parameters, J_1 and the value of the magnetic moment on the Fe atom. Values of $4.3\mu_B$ and $4.5\mu_B$ were estimated, respectively, for the moments in $FeOHSO_4$ and $FeOHCrO_4$. These values are close to the value $(4.55\mu_B)$ determined from neutron diffraction for $FeOHSO_4$.[2] The fit of the susceptibilities of $FeOHCrO_4$ to the linear-chain model at temperatures below 104 K may be fortuitous in view of the three-dimensional magnetic order occurring in this temperature range. The value of J_1 $(-19$ K) determined for $FeOHSO_4$ is close to the value obtained by Scheerlinck and Legrand (20.6 K) (Ref. 2) who fitted the magnetic susceptibility data of Rumbold and Wilson[3] in the higher temperature range ignoring their peak at 56 K.

If we consider only the first three interchain exchange interactions, J_2, J_3, and J_4, we find that the energy eigenvalues for both the $(2\pi,2\pi,0)$ and the $(2\pi,2\pi,2\pi)$ modes contain only terms in J_3 and J_4. Physically, this arises because on the eight atoms contributing to the J_2 interaction, Table I, four spins point in a negative direction and four spins point in a positive direction. Hence the overall (J_2) magnetic exchange interaction at (0,0,0) is zero. The J_3 and J_4 exchange interactions are directed at right angles to the chain direction along the b and c axes, respectively. J_3 is negative in the $(2\pi,2\pi,0)$ mode. Physically, this means that the length of the magnetic cell is double that of the chemical cell in the b-axis direction. However, J_4 is positive [in the $(2\pi,2\pi,0)$ mode] and the magnetic-exchange interaction between chains arises primarily therefore from the difference between J_3 and J_4. From consideration of the superexchange path lengths the value of J_3 is likely to be substantially greater than that of J_4.

We can calculate an average value of the magnetic-exchange interaction between chains for $FeOHSO_4$ and $FeOHCrO_4$ by using Oguchi's results.[17] This method uses two-time and temperature-dependent Green's functions, and calculated magnetizations agree well with spin-wave theory at low temperature and become increasingly similar to results of molecular-field theory at higher temperatures. In this method values of the three-dimensional magnetic-ordering temperature and the magnetic-exchange interaction along the chain are used to calculate a single magnetic-exchange parameter between chains. Hence we can obtain only an average value of the interchain magnetic exchange from his result.

Oguchi's expression for the Néel temperature is[17]

$$\frac{kT_N}{|J_1|}=\frac{4S(S+1)}{3I(\eta)} ,$$

where η is the ratio of inter- to intra-chain magnetic-exchange interaction, and $I(\eta)$ for the (a,b,c) orthorhombic cell is given in our case by

$$I(\eta)=\frac{1}{\pi^3}\int_0^\pi\int_0^\pi\int_0^\pi\frac{dq_x dq_y dq_z}{\eta(1-\cos q_y)+\eta(1-\cos q_z)+1-\cos(q_x/2)} ,$$

where x is taken along the linear chain.

Substituting for T_N, the three-dimensional magnetic-ordering temperatures 111 and 104 K, estimated for $Fe(OH)SO_4$ and $Fe(OH)CrO_4$, respectively, and evaluating the integral numerically, we derive an interchain, magnetic-exchange interaction of $|4|$ K for $Fe(OH)SO_4$ and $|3|$ K for $Fe(OH)CrO_4$.

The values of η (0.2 and 0.1 in $FeOHSO_4$ and $FeOHCrO_4$, respectively) are higher than one might have expected. There are three atoms (O-S-O) intervening between Fe atoms of different chains for the J_3 interaction, and only one oxygen atom (of OH) intervening between adjacent iron atoms in a chain for the J_1 interaction. The J_4 interaction involves four intervening atoms. Each extra atom is expected to diminish the superexchange interaction approximately by an order of magnitude.[18]

In $FeOHCrO_4$ the smaller value of the interchain magnetic exchange interaction, compared to that in $FeOHSO_4$, is reasonable because of the larger orthorhombic cell for the chromate. However, the higher intrachain J_1 value for $FeOHCrO_4$ is not easily understood: The distance between adjacent iron atoms in a chain, 3.75 Å, in $FeOHCrO_4$, is slightly greater than that in $FeOHSO_4$, 3.65 Å. Empty low-lying Cr^{6+} d states in $FeOHCrO_4$ might have been expected to enhance the interchain magnetic-exchange interaction rather than the intrachain interaction because iron atoms in adjacent chains are linked by $(CrO_4)^{2-}$ anions.

There are indications of additional magnetic transitions at about 25 and at 10 K in the susceptibility data for $FeOHSO_4$ and $FeOHCrO_4$, respectively, Fig. 1, but further work would be required to establish their intrinsic nature.

In the Mössbauer spectra of $FeOHSO_4$ at temperatures above 90 K, Fig. 3, and in that of $FeOHCrO_4$ in the same temperature region, Fig. 5, a quadrupole doublet is superimposed on a magnetic hyperfine spectrum. The coexistence of such spectra just below T_N may arise from fluctuations of correlations in or between one-dimensional magnetic chains. Either a magnetic hyperfine spectrum or a quadrupole doublet might be observed depending on the correlation length and on the fluctuation rate compared to the Mössbauer Larmor precession frequency.

The lines in the spectrum of $FeOHCrO_4$ at 4 K, Fig. 6, are fairly narrow and the spectrum is quite well fitted by a single magnetic sextet. In the spectrum of $FeOHCrO_4$ at 4 K in an applied external magnetic field of 40 kOe, Fig. 7, the outside lines are broadened, indicating the antiferromagnetic character of $FeOHCrO_4$.

In contrast, the lines in the spectrum of $FeOHSO_4$ at 4 K, Fig. 4, are broader than those in $FeOHCrO_4$, and there is some indication of another weak magnetic sextet, which may be a small admixture of a second phase in our specimen. The outside lines in $FeOHSO_4$ are again broadened in an external magnetic field showing antiferromagnetic behavior.

The values of θ', the polar angle of the internal magnetic field in the principal axes of the electric field gradient, estimated from the Mössbauer spectra of $FeOHSO_4$ (40°) and $FeOHCrO_4$ (42°) do not appear to correlate closely with the spin-directions determined from neutron diffraction. Summation over the lattice using an ionic point-charge model, shows that the direction of the principal electric field gradient at Fe is along the Fe—OH bond direction. There are two such bond directions in the *b* plane, resulting from two Fe sites in the orthorhombic cell. From our neutron results on $FeOHCrO_4$, we predict $\theta' = 40°$ and 80°. It is possible that the discrepancy with Mössbauer data lies in the unavoidable assumption of $\eta = 0$ in the Mössbauer fit.

The noncollinear magnetic model of Scheerlinck and Legrand[2] for $FeOHSO_4$ below 55 K would require $\theta' = 10°$ and 51° for the spin directions on Fe atoms in one *c* plane and $\theta' = 71°$ and 92° for the spin directions on Fe atoms in the adjacent *c* plane. The breadth of the $FeOHSO_4$ Mössbauer magnetic hyperfine lines might possibly conceal this information but it would need some coincidental variations in magnitudes of quadrupole splitting.

The Mössbauer spectra of $FeOHSO_4$ recorded by Rumbold and Wilson were asymmetric at low temperature.[3] This was interpreted by a theory which took into account admixture of nuclear eigenfunctions by nonparallel magnetic and quadrupolar principal-axes systems.[3] The spectra here, on the other hand, are symmetric and this suggests that the spectra observed by Rumbold and Wilson[3] most probably contained contributions from another phase. Amorphous impurities can sometimes occur in synthetic materials of this type, as discussed above, and may possibly explain the effect observed. Eibschutz and Lines have shown that amorphous materials can show asymmetric Mössbauer spectra because of a positive correlation between the hyperfine parameters.[19]

ACKNOWLEDGMENTS

One of us (M.G.T.) thanks Dr. P. Mangin, Institute Laue-Langevin, Grenoble, for able assistance in recording the neutron-diffraction patterns of $FeOHCrO_4$, and Dr. J. Addison and Dr. W. B. Muir, McGill University, for their magnetic susceptibility data. He wishes to express his thanks to Professor E. F. Bertaut and members of Laboratoire de Crystallographie for their kind hospitality and for their many stimulating discussions during the tenure of a Canada-France NRC exchange.

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[*] Permanent address: Department of Energy, Mines and Resources, 555 Booth Street, Ottawa, Canada.

[1] G. Johansson, Acta Chem. Scand. **16**, 1234 (1962).

[2] D. Scheerlinck and E. Legrand, Physica **86-88B**, 913 (1977).

[3] B. D. Rumbold and G. V. H. Wilson, J. Phys. Chem. Solids **35**, 241 (1974).

[4] A. Bonnin and A. Lecerf, C. R. Acad. Sci. Ser. C **262**, 1782 (1966); R. W. Cattrall, K. S. Murray, and K. L. Peverill, Inorg. Chem. **10**, 1301 (1971).

[5] D. A. Powers, G. R. Rossman, H. J. Schugar, and H. B. Gray, J. Solid State Chem. **13**, 1 (1975).

[6] E. Hermon, R. Haddad, D. J. Simkin, D. E. Brardão, and W. B. Muir, Can. J. Phys. **54**, 1149 (1976).

[7] J. Addison and W. B. Muir (unpublished).

[8] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).

[9] J. C. Bonner, H. W. J. Blote, H. Beck, and G. Muller, in *Physics in One Dimension*, edited by J. Bernasconi and T. Schneider (Springer, Berlin, 1981), p. 115.

[10] *International Tables for X-ray Crystallography*, International Union of Crystallography (Kynoch, Birmingham, UK, 1969).

[11] (a) JCPDS, International Centre for Diffraction Data, Swarthmore, PA, Inorganic phases; (b) *ibid.*, file no. 21-928.

[12] K. Ruebenbauer and T. Birchall, Hyperfine Interact. **7**, 125 (1979).

[13] L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).

[14] L. P. Regnault, Thèse D.E.S., Physique, Université de Grenoble, France (1981).

[15] E. F. Bertaut, *Magnetism III*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963).

[16] E. Posjnak and H. E. Merwin, J. Am. Chem. Soc. **44**, 1965 (1922).

[17] T. Oguchi, Phys. Rev. **133**, A1098 (1964).

[18] J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).

[19] M. Eibschutz and M. E. Lines, Phys. Rev. B **206**, 2288 (1982).