

## Mössbauer study of $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$

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Ferrimagnetic  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  has been investigated over a temperature range from 4.2 to 347 K using the Mössbauer technique. X-ray diffraction shows that it has a cubic spinel structure and a lattice constant of  $a_0 = 8.346 \pm 0.005 \text{ \AA}$ . The isomer shift indicates that iron ions are ferric and located at the tetrahedral sites. Its Néel temperature  $T_N$  is found to be  $343 \pm 2 \text{ K}$ . As the temperature increases toward  $T_N$  a systematic line broadening effect in the Mössbauer spectrum is observed and interpreted to originate from different temperature dependencies of the magnetic hyperfine fields at various iron sites.

### I. INTRODUCTION

The copper chromite  $\text{CuCr}_2\text{O}_4$  is known to have a tetragonal distortion of the spinel arrangement.<sup>1</sup> Its pseudocell containing eight molecules, which is strictly analogous to the spinel cube, has the dimensions<sup>2</sup>  $a_0 = 8.52 \text{ \AA}$  and  $c_0 = 7.80 \text{ \AA}$ . Its metallic atoms are in a normal distribution; the copper ions are in the *A* (tetrahedral) sites and the chromium ions in the *B* (octahedral) sites.  $\text{CuCr}_2\text{O}_4$  is known to be ferrimagnetic with a Néel temperature of 135 K.<sup>2,3</sup> Neutron diffraction experiments<sup>4</sup> show that the magnetic moments of the Cr and Cu atoms are  $3\mu_B$  and  $1\mu_B$ , respectively, implying that Cr and Cu ions are in the charge states of  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$ , respectively.

In this study  $\text{Cr}^{3+}$  ions were progressively replaced by  $\text{Fe}^{3+}$  ions to raise the Néel temperature. When 7 out of 20  $\text{Cr}^{3+}$  ions were replaced by  $\text{Fe}^{3+}$  ions, the crystal structure became a cubic spinel structure and its Néel temperature rose to 343 K. Mössbauer spectra of  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  have been collected over a wide temperature range 4.2–347 K. We note a systematic line broadening effect which increases with increasing temperature and is interpreted to originate from different temperature dependencies of the magnetic hyperfine fields at various iron sites.

### II. EXPERIMENTAL PROCEDURE

The  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  sample was prepared by heating a mixture of the proper proportions of  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{Cr}_2\text{O}_3$  powders of 99.995%, 99.999%, and 99.999% purity, respectively, in an evacuated and sealed quartz ampoule. For the heat treatment, the mixture was fired at 1000 °C for 24 h, next ground, and finally heated again at 1000 °C for 24 h. The sample was  $^{57}\text{Fe}$  enriched to 5 at.% of the metal atoms for Mössbauer measurements. X-ray diffraction patterns showed that the sample had the cubic spinel structure having a lattice constant at room temperature of  $a_0 = 8.346 \pm 0.005 \text{ \AA}$ .

Mössbauer spectra were recorded using a conventional Mössbauer spectrometer of the electromechanical type with  $^{57}\text{Co}$  source in a rhodium matrix.

### III. RESULTS

#### A. Cation distribution

Figures 1 and 2 illustrate the temperature variation of the Mössbauer spectrum. The Mössbauer absorption lines are six in number and sharp at 4.2 K while they broaden increasingly with increasing temperature. Just above the Néel temperature of  $T_N = 343 \pm 2 \text{ K}$ , the

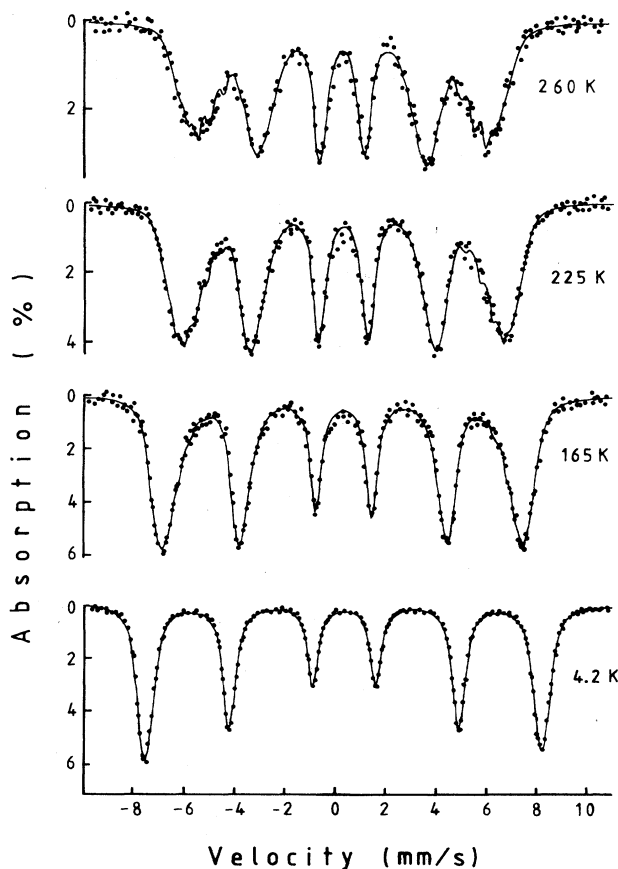


FIG. 1. Mössbauer spectra of  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  at low temperatures.

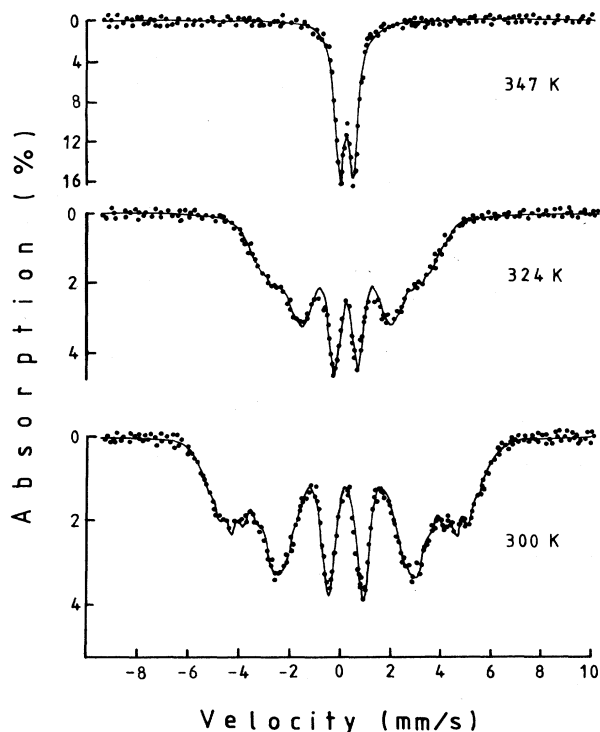
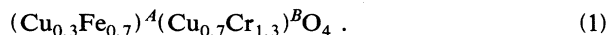


FIG. 2. Mössbauer spectra of  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  near the Néel temperature.

Mössbauer spectrum becomes a sharp doublet.

Table I shows the magnetic hyperfine field, quadrupole shift, and isomer shift at various temperatures. The isomer shift of 0.28 mm/s at room temperature in Table I corresponds to  $\text{Fe}^{3+}$  at *A* sites, because the isomer-shift values at room temperature for the *A* and *B* sites of  $\text{CuCr}_{0.1}\text{Fe}_{1.9}\text{O}_4$  are 0.28 and 0.37 mm/s, respectively.<sup>5</sup> In view of the well-known preference<sup>6</sup> of  $\text{Cr}^{3+}$  ions for the *B* sites one may assume that the cation distribution of  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  is



$$\langle E_Q \rangle = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \frac{1}{8} e^2 q Q [3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos(2\phi)] \sin \theta d\theta d\phi = 0. \quad (4)$$

Thus we can get a vanishing quadrupole shift below  $T_N$  if the magnetic hyperfine field is randomly oriented with respect to the principal axes of the electric-field-gradient tensor.

In the spinel structure of  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$ , each *A*-site  $\text{Fe}^{3+}$  ion is surrounded by four nearest-neighbor oxygen ions and 12 next-nearest-neighbor (NNN) *B*-site ions, which are  $\text{Cu}^{2+}$  or  $\text{Cr}^{3+}$  according to the cation distribution (1). The number of configurations and the probability for  $n$   $\text{Cr}^{3+}$  ions and  $(12-n)$   $\text{Cu}^{2+}$  ions to occupy the 12 NNN *B* sites are

$$N(n) = \binom{12}{n} = \frac{12!}{n!(12-n)!} \quad (5)$$

TABLE I. Average values of magnetic hyperfine field  $H$ , quadrupole shift  $E_Q$ , and isomer shift  $\delta$  for  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  at various temperatures  $T$ .  $\delta$  is relative to the iron metal.

$T$ (K)	$H$ (kOe)	$E_Q$ (mm/s)	$\delta$ (mm/s)
4.2	487	-0.01	0.40
30	482	-0.01	0.40
85	470	-0.01	0.39
165	433	-0.01	0.36
225	377	0.00	0.34
260	340	0.00	0.31
300	268	-0.01	0.28
324	177	0.00	0.26
	( $\pm 2$ )	( $\pm 0.01$ )	( $\pm 0.01$ )

### B. Quadrupole splittings

Above the Néel temperature  $T_N$ , the quadrupole splitting is given by

$$\epsilon = \frac{1}{2} e^2 q Q (1 + \frac{1}{3} \eta^2)^{1/2}. \quad (2)$$

The value of  $\epsilon$  was found to be  $0.54 \pm 0.01$  mm/s at 347 K which is just above  $T_N$ . On the other hand, Table I shows that all the quadrupole shift values,  $E_Q$ , are zero below  $T_N$  within experimental error. These seemingly contradictory phenomena may be explained as follows.

When the quadrupole interaction is much weaker than the magnetic hyperfine interaction, the Mössbauer line shift from the quadrupole interaction can be described by

$$E_Q = \frac{1}{8} e^2 q Q [3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos(2\phi)], \quad (3)$$

where  $\theta$  and  $\phi$  are the angles, in polar coordinates, between the magnetic hyperfine field vector and the principal axes of the electric-field-gradient tensor. On assuming that the maximum electric field gradient  $q$  and the asymmetry parameter  $\eta$  are independent of  $\theta$  and  $\phi$ , the average value of  $E_Q$  taken over all directions vanishes; viz.,

and

$$P(n) = \binom{12}{n} \left[ \frac{1.3}{2} \right]^n \left[ \frac{0.7}{2} \right]^{12-n}, \quad (6)$$

respectively. Table II shows the calculated values of  $N(n)$  and  $P(n)$ .  $n$  values for which  $P(n)$  exceeds 4% are 5, 6, 7, 8, 9, and 10; the corresponding  $N(n)$  values of 495, 792, 924, 792, 495, 220, and 66 may be large enough to make  $\theta$  and  $\phi$  random, thereby leading to Eq. (4).

### C. Line broadening

As can be seen in Figs. 1 and 2, the Mössbauer absorption lines broaden increasingly as the temperature ap-

TABLE II. The number of ways  $N(n)$  and the probability  $P(n)$  for  $n$  Cr ions and  $(12-n)$  Cu ions to be distributed among the 12 next-nearest-neighbor  $B$  sites of a Fe ion.

$n$	$N(n)$	$p(n)$
0	1	0.000
1	12	0.000
2	66	0.001
3	220	0.005
4	495	0.020
5	792	0.059
6	924	0.128
7	792	0.204
8	495	0.237
9	220	0.195
10	66	0.109
11	12	0.037
12	1	0.006

proaches the Néel temperature  $T_N$  from below. This kind of line broadening may be ascribed to the superparamagnetic effects;<sup>7</sup> as the temperature of the sample is raised to  $T_N$ , the anisotropy energy decreases to zero, and thus magnetization reversals of comparatively large volumes may be thermally excited. In such a case, as the temperature approaches  $T_N$ , the spin-flip frequency of the magnetic moment in superparamagnetic fine particles increases, thereby giving rise to the simultaneous presence of a broadened hyperfine structure and a strong central peak in the Mössbauer spectrum.<sup>7</sup> Absence of a central single-line peak in Figs. 1 and 2 rules out the superparamagnetic effects.

The asymmetric broadening of the Mössbauer spectral lines may result from the multitude of possible environments for an iron nucleus.<sup>8</sup> As shown in Table II, there are 13 possible magnetic environments for Fe ions in  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$ ; those for  $n=5, 6, 7, 8, 9$ , and 10 have significantly large probabilities  $P(n)$ . The hyperfine fields at Fe nuclei in different environments may have different temperature dependence, thereby giving rise to asymmetric line broadening in the Mössbauer spectra.

The molecular field acting on  $\text{Fe}^{3+}$  ions with  $n$  NNN  $\text{Cr}^{3+}$  may be approximated by

$$H(n) = -\frac{2}{g\mu_B} J_n \langle \bar{S}' \rangle. \quad (7)$$

Here,  $J$  is an exchange integral between  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions,  $\mu_B$  is the Bohr magneton,  $\langle \bar{S}' \rangle$  is the average value of the chromium ion spin taken over all environments, and  $\bar{S}'$  is the average value of  $S'_z$  for a particular environment.  $g$  is the  $g$  factor of a  $\text{Fe}^{3+}$  ion.

On the other hand, each  $B$ -site  $\text{Cr}^{3+}$  ion is surrounded by six nearest-neighbor oxygen ions and 6 next-nearest-neighbor  $A$ -site ions, which are  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  according to the cation distribution (1). The probability for  $n'$   $\text{Fe}^{3+}$  ions and  $(6-n')$   $\text{Cu}^{2+}$  ions to occupy the 6 NNN  $A$  sites is

$$P'(n') = \binom{6}{n'} (0.7)^{n'} (0.3)^{6-n'}. \quad (8)$$

The molecular field acting on  $\text{Cr}^{3+}$  ions with  $n'$  NNN

$\text{Fe}^{3+}$  ions is also approximated by

$$H'(n') = -\frac{2}{g'\mu_B} J_{n'} \langle \bar{S} \rangle, \quad (9)$$

where  $S$  stands for the  $\text{Fe}^{3+}$  spin, and  $g'$  is the  $g$  factor of a  $\text{Cr}^{3+}$  ion.

It is true that the approximations given by Eqs. (7) and (9) are somewhat crude, because all the intrasublattice exchange interactions and all the  $A$ - $B$  interactions involving copper ions are neglected. However, the intrasublattice interactions in ferrimagnetic oxyspinels are considerably weaker than  $A$ - $B$  interactions,<sup>9</sup> and  $J_{A-B}$  values involving copper ions are supposed to be smaller in magnitude than  $J_{\text{Fe-Cr}}$  because the Néel temperature of 135 K for  $\text{CuCr}_2\text{O}_4$  is much lower than 343 K for  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$ . Now the average value of the  $z$  component of a  $\text{Fe}^{3+}$  spin  $S$  with  $n$  NNN  $\text{Cr}^{3+}$  ions can be written as

$$\bar{S}(n) = -SB_S \left[ \frac{g\mu_B SH(n)}{k_B T} \right], \quad (10)$$

and its average value over all environments is

$$\langle \bar{S} \rangle = \sum_{n=0}^{12} P(n) \bar{S}(n), \quad (11)$$

where  $B_S(x)$  is the Brillouin function for a spin  $S$ .  $k_B$  and  $T$  represent the Boltzmann constant and temperature, respectively. Similarly, the average value of the  $z$  component of a  $\text{Cr}^{3+}$  spin  $S'$  with  $n'$  NNN  $\text{Fe}^{3+}$  ions can be written as

$$\bar{S}'(n') = -S'B_{S'} \left[ \frac{g'\mu_B S'H'(n')}{k_B T} \right], \quad (12)$$

and its average value over all environments is

$$\langle \bar{S}' \rangle = \sum_{n'=0}^6 P'(n') \bar{S}'(n'). \quad (13)$$

The magnetic ordering temperature can be easily derived from Eqs. (10) through (13) to be

$$T_N = \frac{2|J|}{3k_B} [S(S+1)S'(S'+1)\langle n \rangle \langle n' \rangle]^{1/2}, \quad (14)$$

where  $\langle n \rangle$  and  $\langle n' \rangle$  are given by

$$\langle n \rangle = \sum_n nP(n) \text{ and } \langle n' \rangle = \sum_{n'} n'P'(n'). \quad (15)$$

Now it is convenient to introduce the reduced variables

$$\sigma(n) = \bar{S}(n)/S, \quad \sigma'(n') = \bar{S}'(n')/S'$$

and

$$\tau = T/T_N. \quad (16)$$

Then Eqs. (10) through (13) are now combined to give the equations of state:

$$\sigma(n) = -B_S \left[ na \sum_{n'} P'(n') \sigma'(n') / \tau \right], \quad (17)$$

$$\sigma'(n') = -B_{S'} \left[ n'a \sum_n P(n) \sigma(n) / \tau \right], \quad (18)$$

where  $a$  is a constant given by

$$a = 3SS' / [S(S+1)S'(S'+1)\langle n \rangle \langle n' \rangle]^{1/2}. \quad (19)$$

For each reduced temperature  $\tau$ , the reduced spins  $\sigma(n)$  and  $\sigma'(n')$  of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  in different environments are calculated numerically by solving Eqs. (17) and (18) simultaneously. Figure 3(a) shows the temperature dependence of  $\sigma(n)$  for various  $n$  values with corresponding  $P(n)$  values greater than 1%. Figure 3(b) represents the spread  $\Delta\sigma$  of  $\sigma(n)$  values relative to the average value  $\langle \sigma \rangle$  as a function of  $\tau$ :

$$\Delta\sigma = (\langle \sigma^2 \rangle - \langle \sigma \rangle^2)^{1/2}, \quad (20)$$

where

$$\langle \sigma \rangle = \sum_n \sigma(n)P(n)$$

and

$$\langle \sigma^2 \rangle = \sum_n \sigma^2(n)P(n). \quad (21)$$

It can be noted in Fig. 3 that  $\sigma(n)$  values spread widely as the temperature increases toward  $T_N$ .

The magnetic hyperfine field at  $\text{Fe}^{3+}$  with  $n$  NNN  $\text{Cr}^{3+}$  ions can be taken to be  $H_0(n)\sigma(n)$ , where  $H_0(n)$  represent the magnetic hyperfine field at 0 K and may be written as  $H_0 + n \Delta H$ .<sup>10</sup>  $H_0$  and  $\Delta H$  were obtained to be 429.9 and 7.4 kOe, respectively, by fitting thirteen sets of 6-Lorentzian-line patterns with relative intensities  $P(n)$  to the Mössbauer spectrum at 4.2 K. In this fit, a single set of quadrupole shift  $E_Q$  and isomer shift  $\delta$  was used as free parameters. Even though Eq. (4) indicates  $\langle E_Q \rangle = 0$ , the line broadening due to the random orientation of  $(\theta, \phi)$  in  $E_Q$  is not zero; that is,<sup>11</sup>

$$\begin{aligned} 2(\langle E_Q^2 \rangle - \langle E_Q \rangle^2)^{1/2} &= \frac{1}{\sqrt{5}} \frac{e^2qQ}{2} (1 + \frac{1}{3}\eta^2)^{1/2} \\ &= \frac{1}{\sqrt{5}} 0.54 = 0.24 \text{ mm/s}, \end{aligned} \quad (22)$$

which was added to the natural linewidth of each Lorentzian line in the analysis. For all the other temperatures below  $T_N$ , Mössbauer spectra were fitted in the same way as that for 4.2 K except that  $(H_0 + n \Delta H)\sigma(n)$  instead of  $H_0 + n \Delta H$  was used for the magnetic hyperfine fields. The solid lines over the data points in Figs. 1 and 2 represent the results of this fitting, and Table I lists the average magnetic hyperfine field, quadrupole shift, and isomer shift at each temperature. The fairly good agree-

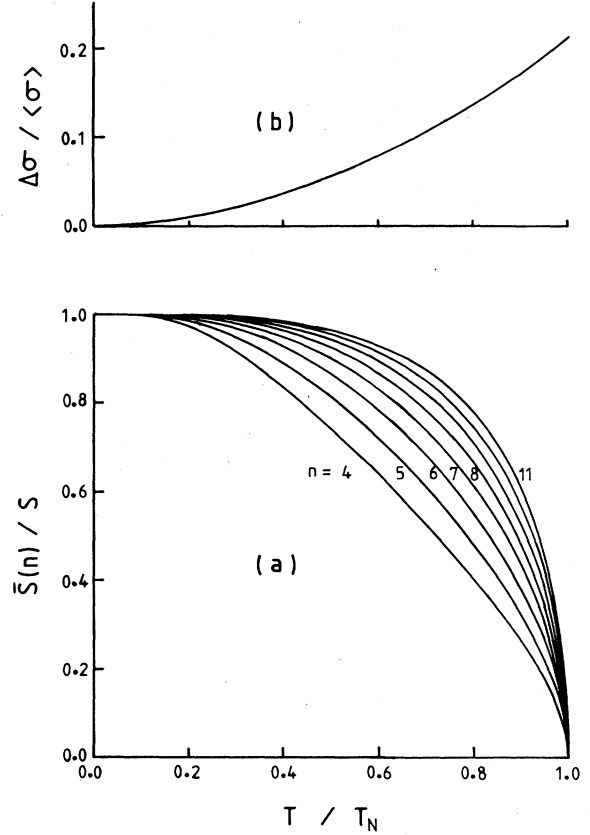


FIG. 3. (a) Reduced spin vs reduced temperature for  $\text{Fe}^{3+}$  with  $n$  next-nearest neighbor  $\text{Cr}^{3+}$ . (b) Spread  $\Delta\sigma$  of the reduced spin divided by the average value  $\langle \sigma \rangle$  of the reduced spins as a function of reduced temperature.

ment between the theoretical curve and the data points in Figs. 1 and 2 suggests that the asymmetric line broadening in the Mössbauer absorption lines of  $\text{CuFe}_{0.7}\text{Cr}_{1.3}\text{O}_4$  observed below  $T_N$  originates from different temperature dependencies of the magnetic hyperfine fields at various iron sites.

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