Mössbauer study of $CuCr_{0.1}Fe_{1.9}O_4$

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$CuCr_{0.1}Fe_{1.9}O_4$ has been studied by Mössbauer spectroscopy and x-ray diffraction. The crystal structure is found to be a tetragonal spinel with the lattice parameters $a_0 = 5.843$ Å and $c_0 = 8.578$ Å. The Mössbauer spectra consist of two six-line patterns corresponding to Fe^{3+} at the tetrahedral (A) and octahedral (B) sites. Debye temperatures for A and B sites are found to be 677 ± 5 and 288 ± 5 K, respectively. The intensity ratio of the A to B patterns is found to increase at low temperatures with increasing temperature due to the large difference of Debye temperatures of the two sites and to decrease at high temperatures due to migration of Fe^{3+} ions from A sites to B sites.

I. INTRODUCTION

The copper ferrite $CuFe_2O_4$ is known to have the hausmannite structure,[1] which is a tetragonal distortion of the spinel arrangement. Its lattice parameters[1] are $a_0 = 5.873$ Å and $c_0 = 8.555$ Å. Its metallic atoms are in an inverse distribution; half the atoms of iron are in the A (tetrahedral) sites and the other half plus the copper atoms in the B (octahedral) sites. X-ray and magnetic studies[2,3] report that the cationic distribution of the copper ferrite can be expressed as

$$(Cu_xFe_{1-x}{}^{3+})^A(Cu_{1-x}Fe_{1+x}{}^{3+})^B O_4$$

with x values ranging from 0.1 to 0.14. However, a recent Mössbauer study[4] shows that tetragonal $CuFe_2O_4$ is an inverse spinel ($x=0$).

In this paper we present our Mössbauer results on tetragonal $CuCr_{0.1}Fe_{1.9}O_4$ with special emphasis on atomic migration as a function of temperature.

II. EXPERIMENTAL PROCEDURE

The $CuCr_{0.1}Fe_{1.9}O_4$ samples were synthesized by the usual ceramic method. A mixture of the proper proportions of Fe_2O_3, CuO, and Cr_2O_3 powders of 99.995%, 99.999%, and 99.999% purities, respectively, was ground, pressed into a pellet at 60 000 N/cm², and sealed in an evacuated quartz tube. The sealed mixture was heated at 1000 °C for 12 h and cooled down slowly. The product was reground, refired at 1000 °C for 12 h, and allowed to cool slowly to room temperature. One of the samples was ^{57}Fe enriched to 5 at. % of the metal atoms for Mössbauer measurements. X-ray diffraction patterns showed that the samples had the tetragonal structure having lattice constants at room temperature of $a_0 = 5.843\pm0.005$ Å and $c_0 = 8.578\pm0.005$ Å.

A Mössbauer spectrometer of the electromechanical type manufactured by Austin Science Associates was used in the constant-acceleration mode. A ^{57}Co source in a rhodium matrix was used at room temperature. To produce a uniform thickness over the area of the Mössbauer absorber, each sample was mixed with boron nitride powder and clamped between two thin boron nitride plates. The absorber thickness was approximately 0.25 mg/cm² of ^{57}Fe.

III. RESULTS

Figure 1 illustrates the temperature variation of the Mössbauer spectra, which are composed of two six-line hyperfine patterns A and B. Using a least-squares computer program, two sets of six Lorentzian lines were fitted to the Mössbauer spectra under the usual restraints,[5] which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction.

The isomer-shift values at room temperature for the A and B patterns are found to be 0.28 ± 0.01 and 0.37 ± 0.01 mm/s relative to the Fe metal, respectively, which are consistent with Fe^{3+}. Figure 2 shows the temperature dependence of the quadrupole shifts. It can be seen in Fig. 2 that the quadrupole shift for the A pattern is much smaller in magnitude than that for the B pattern. This suggests that the A and B patterns originate from the A (tetrahedral) and B (octahedral) sites, respectively, because the local symmetry of the A sites is close to cubic T_d while that of the B sites is close to trigonal D_{3d}. This assignment of the two patterns to the two sites is also consistent with the site assignments[4,6] reported for $CuFe_2O_4$. It is also noteworthy in Fig. 2 that quadrupole shifts decrease substantially in magnitude near 370 K, suggesting a change of the crystal symmetry. A similar change[7] in quadrupole splitting was also observed for $CuFe_2O_4$ and interpreted as arising from tetragonal-to-cubic transformation near 373 K. In order to check this point, x-ray diffraction patterns of $CuCr_{0.1}Fe_{1.9}O_4$ were
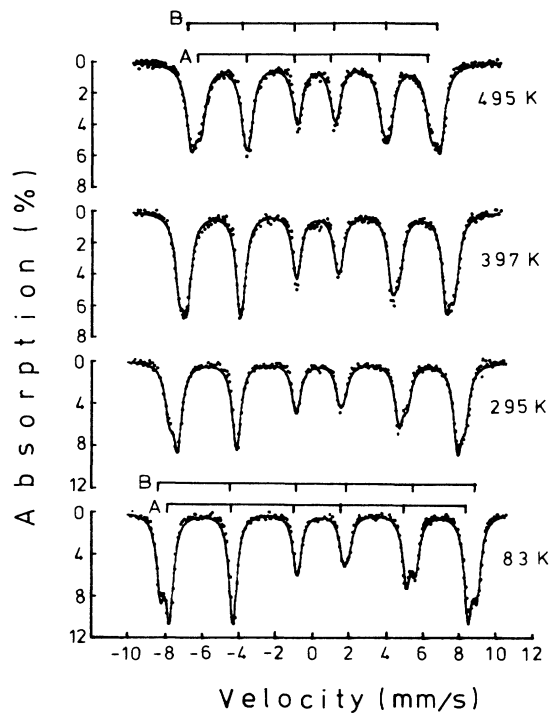
FIG. 1. Mössbauer spectra of $CuCr_{0.1}Fe_{1.9}O_4$ at various temperatures.

taken at 350 and 400 K. It turns out that the crystal structure at 350 K is tetragonal while that at 400 K is cubic.

Figure 3 shows the temperature dependence of the magnetic hyperfine fields of sites A and B. The field values at 83 K for A and B sites are found to be 504 ± 2 and 534 ± 2 kOe, respectively, which are typical values
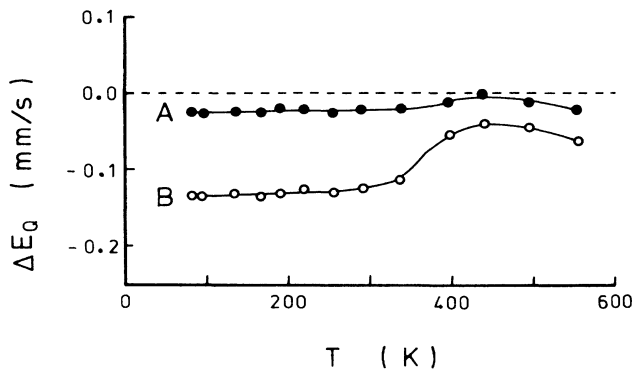

FIG. 2. Temperature dependence of the quadrupole shifts of $CuCr_{0.1}Fe_{1.9}O_4$. The quadrupole shift ΔE_Q is calculated from the expression $\Delta E_Q=(E_1-E_2-E_5+E_6)/4$, where E_i stands for the line position of the ith absorption line in a six-line pattern.
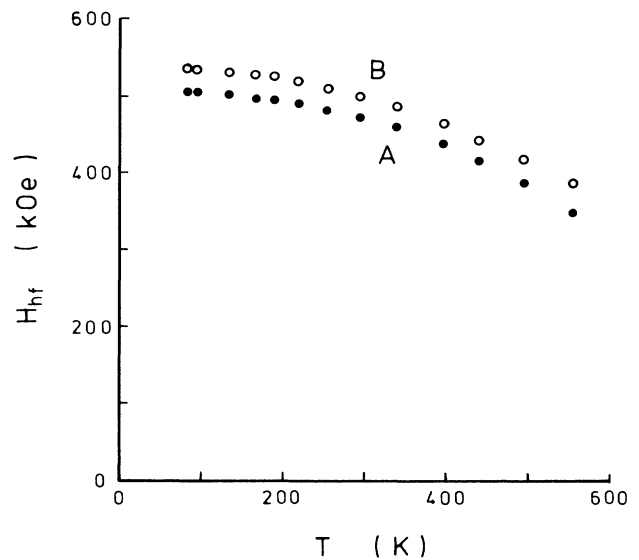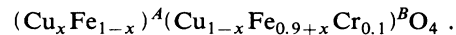

FIG. 3. Temperature dependence of the magnetic hyperfine fields of $CuCr_{0.1}Fe_{1.9}O_4$.

for Fe^{3+} ions. Figure 4 shows the temperature dependence of the absorption area ratio of the A pattern to the B pattern. It is noteworthy in Fig. 4 that the area ratio increases at low temperatures with increasing temperature and then decreases at high temperatures. The reversal of the relative intensities of the A and B patterns at low and high temperatures is evident in Fig. 1. In view of the well-known preference[8] of Cr^{3+} ions for the octahedral sites one may assume that the cation distribution of $CuCr_{0.1}Fe_{1.9}O_4$ is

$$(Cu_xFe_{1-x})^A(Cu_{1-x}Fe_{0.9+x}Cr_{0.1})^BO_4 .$$

The area ratio of the A and B subspectra for the above distribution is

$$\frac{I_A}{I_B}=\frac{(1-x)f_A}{(0.9+x)f_B} , \tag{1}$$

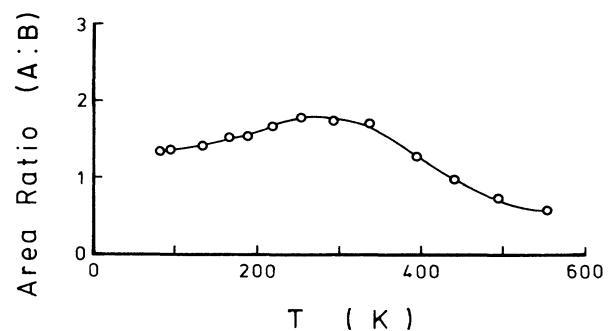where f_A and f_B represent the recoil-free fractions of

FIG. 4. Temperature dependence of the area ratio of the A to B patterns for $CuCr_{0.1}Fe_{1.9}O_4$.

A- and B-site Fe ions, respectively. The Debye model gives the following expression for the recoil-free fraction,[9]

$$f = \exp\left[-\frac{3E_R}{2k_B\Theta}\left[1 + \frac{4T^2}{\Theta^2}\int_0^{\Theta/T}\frac{x\,dx}{e^x - 1}\right]\right], \quad (2)$$

where E_R is the recoil energy of ^{57}Fe for the 14.4-keV gamma ray. Θ and k_B represent Debye temperature and Boltzmann constant, respectively. Heberle[10] has shown that the integral in Eq. (2) can be approximated by the following formula with an error less than 0.1% for $0 < T \leq 0.59\Theta$:

$$\int_0^\Theta \frac{x\,dx}{e^x - 1} = \frac{\pi^2}{6} + \frac{\Theta}{T}\ln(1 - e^{-\Theta/T}) - e^{-\Theta/T} - (e^{\Theta/T}/2)^2 \ . $$

$$(3)$$

Substituting Eq. (3) into (2) and taking the logarithm of both sides, one can get

$$\ln f = \frac{-3E_R}{2k_B\Theta} - \frac{6E_R T^2}{k_B\Theta^3}\left[\frac{\pi^2}{6} + \frac{\Theta}{T}\ln(1 - e^{-\Theta/T})\right.$$

$$\left. - e^{-\Theta/T} - (e^{-\Theta/T}/2)^2 \right] . \quad (4)$$

When $\ln f$ is plotted as a function of T^2, one will get a curve which becomes almost a straight line at low temperatures. Figure 5 shows the logarithms of the absorption areas of the A and B patterns at low temperatures as functions of T^2, which are almost straight lines. Equation (4) with a proper additive constant was fitted to the data in Fig. 5, using a least-squares computer program to get the following Debye temperatures: $\Theta_A = 677 \pm 5$ K and $\Theta_B = 288 \pm 5$ K. If Θ_B is much less than Θ_A, it is evident from Eq. (2) that f_B decreases much more rapidly with increasing temperature than f_A. In other words, f_A/f_B will increase with increasing temperature, thus explaining the tendency of the area ratio to increase with increasing temperature at low temperatures as shown in Fig. 4.
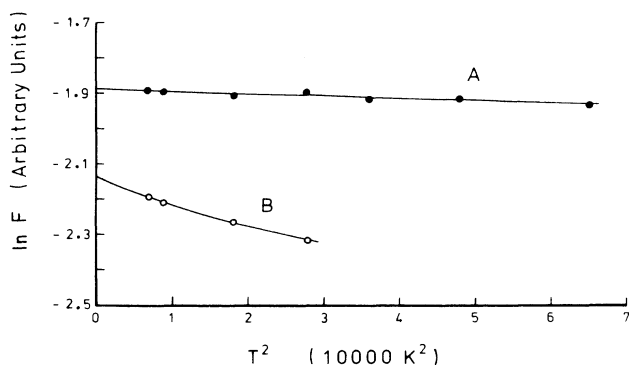
The tendency of the area ratio to decrease at high temperatures in Fig. 4 can be explained in terms of migration of Fe ions from A sites to B sites (in this case, the same number of Cu ions move from B sites to A sites); in other words, an increase of x value in Eq. (1) will result in a decrease of the area ratio. Substituting the experimental area ratios in Fig. 4, and f values of Eq. (2) into Eq. (1), one can get the x values as a function of temperature which are shown in Fig. 6. It can be seen in Fig. 6 that atomic migration starts near room temperature and increases with increasing temperature to such a degree that about 60% of the iron ions at the A sites move over to the B sites at 550 K. The x values in Fig. 6 should be taken with some reservations, because once atomic migration starts Debye temperatures may change. However, no drastic changes of Θ values are expected to take place, because the nearest neighbors of iron ions are oxygen ions instead of metallic ions, and the tetragonality ratio $(c_0 - a_0')/a_0'$ for the pseudocubic cell $(a_0' = \sqrt{2}a_0)$ of $CuCr_{0.1}Fe_{1.9}O_4$ at room temperature is only 0.038. In order to know whether Fig. 6 represents equilibrium concentrations, two Mössbauer spectra were taken with a time separation of 10 hs at 400 K and both spectra gave the same results, thereby indicating that Fig. 6 shows equilibrium values. We also found the same results on lowering and raising the temperature.

Bertaut[11] observed similar atomic migration in $CuFe_2O_4$ by using the x-ray diffraction technique. However, his results show that only 26% of the iron ions at the A sites move over to the B sites at 700 °C. Comparison of our results for $CuCr_{0.1}Fe_{1.9}O_4$ with Bertaut's results for $CuFe_2O_4$ suggests that even a small concentration of Cr ions can change the site preference of Cu^{2+} and Fe^{3+} ions drastically. Sawatzky and co-workers[12] obtained Mössbauer spectra of Fe_3O_4 in the temperature range 300–800 K and found that the Debye temperatures for tetrahedral and octahedral sites were $\Theta_A = 334 \pm 10$ K and $\Theta_B = 314 \pm 10$ K, respectively. Our results on $CuCr_{0.1}Fe_{1.9}O_4$ are in marked contrast with their results. However, they used the following expres-

FIG. 5. Natural logarithm of the absorption area, F, vs T^2 for the A and B subspectra of $CuCr_{0.1}Fe_{1.9}O_4$ at low temperatures.
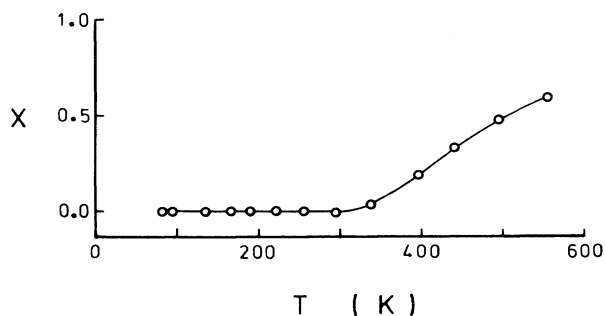

FIG. 6. Temperature dependence of the fraction of tetrahedral sites occupied by the copper ions.

sion for the recoil-free fraction,

$$f = \exp\left[-\frac{6E_R T}{k_B \Theta^2} \right], \qquad (5)$$

which holds for $T \gg \Theta$, while we used Eq. (4). Furthermore, iron ions in tetrahedral and octahedral sites in Fe_3O_4 are Fe^{3+} and $Fe^{2.5+}$, respectively, whereas all iron ions in $CuCr_{0.1}Fe_{1.9}O_4$ are Fe^{3+}.

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