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Jahn–Teller-type crystal distortions in copper ferrite

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The Mössbauer spectra of tetragonal copper ferrite are investigated between 298 and 613 K. The spectra consist of a super-position of two six-line patterns corresponding to Fe^{3+} at the B site (pattern I) and A site (pattern II) of the crystal structure on the basis of their relative isomer shifts, hyperfine fields and quadrupole interactions. The intensity ratio of the two patterns agree to within 15% error with the ratio of Fe site occupancy factors determined by X-ray diffraction methods. The temperature variations of isomer shifts and quadrupole interactions show a sudden change in the temperature region 350 to 425 K for both sites which is an indication of a transition. This transition has been identified to be a non-cubic to tetragonal one and it is due to co-operative Jahn–Teller-type crystal distortions.

1. Introduction

Magnetostriction measurements [1] of slowly cooled and quenched (997 K) copper ferrite samples show transitions around 423 and 373 K, respectively, which are attributed to Jahn–Teller-type crystal distortions. A similar transition was observed by Yamada and Mitui [2] for a quenched (923 K) copper ferrite sample at 363 K which was found to be a cubic to tetragonal transition. This ferrite has also been studied by Evans and Hafner [3] using high magnetic fields, and they suggest that metastable cubic phases may even exist at lower temperatures. However, the intensity ratio of the two sites found by Evans and Hafner [3] was a factor of two off from the X-ray diffraction measurements [4–6]. In order to investigate metastable transition at lower temperatures and to relate this transition to Jahn–Teller-type crystal distortions, we undertook a Mössbauer study of slowly cooled copper ferrite as a function temperature.

2. Experimental details

Polycrystalline $CuFe_2O_4$ samples were prepared by intimately mixing Fe_2O_3 and CuO powders in a 1:1 mole ratio and fired at 900° C for 48 h in air and slowly cooled to room temperature. Axial ratio c/a of this specimen was obtained by means of X-ray diffraction, which happens to be 1.06. The Mössbauer absorber was prepared by pressing a powdered sample between two very thin aluminium foils, and the thickness of the absorber was between 10 and 20 mg cm^{-2}.

The Mössbauer spectrometer was of a constant velocity type equipped with a source of 3.5 mC ^{57}Co diffused in a copper matrix. The 14.4 keV gamma rays were detected with a xenon–methane filled propertional counter. The data accumulation was done with the aid of an automatic printer.

A furnace consisting of Nichrome wires wound on a copper strip with a hole to mount an absorber, was used to vary the temperature of the absorber above room temperature. The whole system was kept in a vacuum of the order of 10^{-4} mm Hg. The temperature of the absorber was measured and regulated through a chrome–alumel thermocouple with an accuracy of ± 1 K.

3. Results and discussion

A typical room temperature Mössbauer spectrum of $CuFe_2O_4$ is shown in Fig. 1a, which is not a simple six-line pattern, but consists of two six-line patterns of non-equivalent sites superimposed on each other. The high temperature Mössbauer spectra of $CuFe_2O_4$ were obtained in the tempera-

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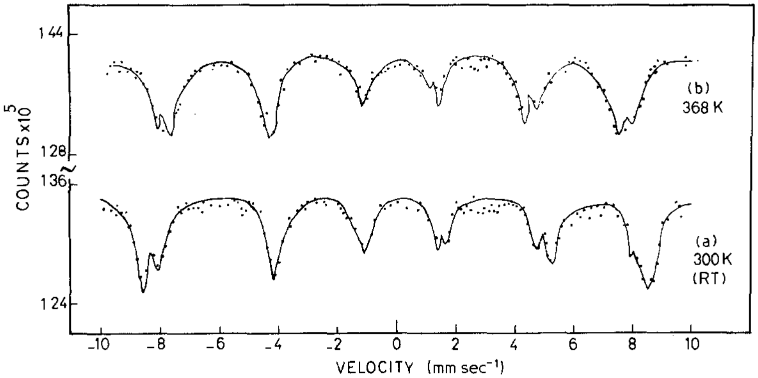

Figure 1 Mössbauer spectra of tetragonal $CuFe_2O_4$ at (a) room temperature (300 K), and (b) 368 K.

ture range 298 to 613 K. These spectra were analysed by a superposition of two six-line patterns (I and II). Patterns I and II, respectively, correspond to Fe^{3+} at the B site (octahedral configuration) and Fe^{3+} at the A site (tetrahedral configuration). These sites were identified on the bases of measured hyperfine fields. Fig. 2 shows the temperature dependence of the hyperfine fields of sites I and II. It is an established fact that the hyperfine field at the octahedral site B should be greater than that at the tetrahedral site A.

The isomer shift (δ), quadrupole splitting (ΔS), and hyperfine field (H) for the two sites obtained from the room temperature spectrum are listed in Table I together with earlier results [3]. Our results agree fairly well with the previous measurements [3] which suggests that the two sites have been assigned properly. The presently observed intensity of octahedral site B is greater than that of tetrahedral site A in accordance with X-ray diffraction values [4–6]. However, Evans and Hafner [3] have observed greater intensity for tetrahedral site A than octahedral site B. The cationic distribution of the copper ferrite is expressed as

$$(Cu_x Fe^{3+}_{1-x})^A [Cu_{1-x} Fe^{3+}_{1+x}]^B O_4.$$

The area ratio of the octahedral to the tetrahedral Mössbauer pattern is equal to $1 + x/1 - x$, which in the present work is 1.56. This ratio gives a value of 0.22 for x.

The fraction x obtained from X-ray diffraction patterns [4, 5] and magnetization measurements [6] has been reported to have a value ranging from 0.1 to 0.14 for tetragonal phases with the same c/a ratio (1.06) as the present sample. These values of x give ratio I/II between 1.22 and 1.33 which agrees with our value of 1.56 within about 15% error. This shows that the present relative intensity corresponds very well to Fe^{3+} site occupancy factors determined by X-ray diffraction patterns and magnetization measurements. On the contrary, the ratios obtained by Evans and Hafner [3] range from 0.6 to 0.7 for the single crystal and ceramic specimen, respectively, which is about a factor of two smaller than the present value and X-ray work [4–6].

The variation of isomer shift with temperature is shown in Fig. 3 for the two sites. The pattern with larger hyperfine field exhibits larger isomer shift which is consistent with the nearly general correlation between fields and shift in ferrites. But it is observed in the present work (Fig. 3) that the isomer shifts for the two sites suddenly change

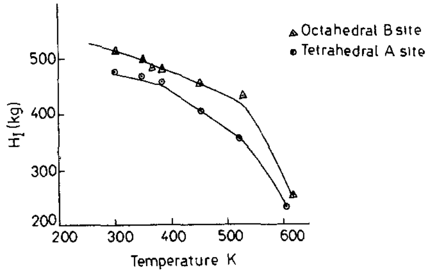

Figure 2 The temperature variation of the hyperfine fields of tetragonal $CuFe_2O_4$.

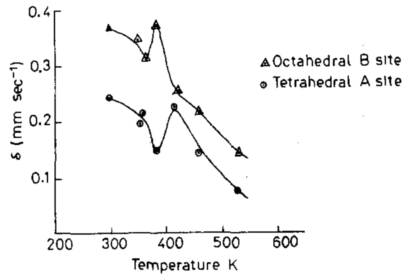

Figure 3 Temperature dependence of the isomer shifts of tetragonal $CuFe_2O_4$.

TABLE I

	A site			B site			Site occupancy ratio I/II
	H_I (kg)	δ^* (mm sec^{-1})	ΔS (mm sec^{-1})	H_I (kg)	δ^* (mm sec^{-1})	ΔS (mm sec^{-1})	
Present work	477 ± 3	0.243 ± 0.024	−0.195 ± 0.045	513 ± 3	0.365 ± 0.025	−0.683 ± 0.045	1.56 ± 0.020
Evans and Hafner [3]	484 ± 2	0.26 ± 0.02	−0.03 ± 0.01	512 ± 2	0.37 ± 0.02	−0.70 ± 0.03	0.70 ± 0.05

*With respect to iron metal.

around 368 K which suggests a sort of metastable transition. A close look at the transition region 350 to 425 K shows that the isomer shift suddenly decreases around 368 K and then increases for the two sites. It is interesting to note that even at the transition region, i.e. 368 K, the two sites are still distinct as shown in Fig. 1b. This fact suggests that this transition is not a cubic to tetragonal one but corresponds to something else. We attribute this transition to co-operative Jahn–Teller-type crystal distortions due to the presence of Cu^{2+} ions in $CuFe_2O_4$.

Further support for this transition has also been observed in the temperature variation of quadrupole interactions (Fig. 4). It is evident from Fig. 4 that the presence of a dip around 368 K in the temperature variation of quadrupole interaction for each site corresponds to the above-mentioned transition.

The presently found transition for the slowly cooled copper ferrite sample is entirely different from that of Yamada and Mitu [2], because they observed a cubic to tetragonal transition for a quenched sample, whereas we have seen a non-cubic to tetragonal transition for the slowly cooled sample. The transition observed in this work between 350 and 425 K corresponds to an anomaly around 423 K seen in magnetostriction measurements [1] of the slowly cooled sample. According to Miyadai and Seino [1], this anomaly arises due to Jahn–Teller-type crystal distortions and our Mössbauer study confirms its existence.

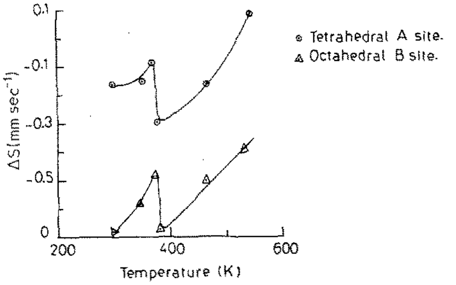

Figure 4 The temperature variation of the quadrupole interaction ΔS, of tetragonal $CuFe_2O_4$.

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