$CuFe_2O_4$ THIN FILMS: HYPERFINE INTERACTIONS OF ^{57}Fe NUCLEI AND DISTRIBUTION OF CATIONS

J. Kohout[1]*, T. Kmječ*[1]*, M. Kučera*[1]*, K. Závěta*[1]

[1] *Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2,*
Prague 8, CZ 180 00

E-mail: kohout@mbox.troja.mff.cuni.cz

Received 30 April 2016; accepted 16 May 2016

Abstract

Sputter-deposited copper ferrite ($CuFe_2O_4$) films can be stabilized in cubic or tetragonal structures depending on the deposition conditions and post-deposition heat treatment [1]. The difference is explained by redistribution of cations over particular crystal sites and a distortion of the spinel lattice due to the Jahn-Teller effect of Cu^{2+} ions.

Here we report hyperfine parameters of ^{57}Fe nuclei in octahedral and tetrahedral iron sites and occupancy of Cu^{2+} ions in tetrahedral sites of $CuFe_2O_4$ (can be considered in principle as an inverse spinel) derived by Mössbauer spectroscopy.

1. Introduction

Bulk copper ferrite crystallizes in a classic spinel structure and may exist in two symmetry modifications, cubic with space group $Fd3m$ at temperature $T_v > 700$ K (427°C) and lattice parameter $a = 8.41624(2)$ Å at 773 K (500°C) and tetragonal with space group $I41/amd$ below T_v and lattice parameter $a = 5.81227(4)$ Å, $c = 8.7115(1)$ Å at 293K (20°C) derived from neutron diffraction [2].

Copper ferrite of nominal composition $CuFe_2O_4$ can be generally described by the structural formula:

$$\left(Cu_{\delta}Fe_{1-\delta}\right)^{A}\left[Cu_{1-\delta}Fe_{1+\delta}\right]^{B}O_4 \qquad (1)$$

where parentheses and square brackets denote the tetrahedral A-sites and octahedral B-sites, respectively and parameter δ is the fraction of Cu ions in tetrahedral A-sites. Although Cu-ferrite can be considered in principle as an inverse spinel[3], however, some of Cu^{2+} ions at room temperature also occupy the tetrahedral sites, $\delta\sim 0.06$ [2]. The degree of inversion may change during the transition from the cubic to tetragonal phase, and it is known to depend on the cooling rate [4]. The cooperative Jahn-Teller effect, arising from the octahedral cupric Cu^{2+} ions, leads to the elongation of the octahedron and the spinel lattice is tetragonally distorted. It is generally accepted to consider the transition to the tetragonal phase as a compression or elongation along one of cubic axes, due to which the structure becomes tetragonal with space group $F4_1/ddm$ and lattice parameter $a' = a\sqrt{2} = 8.21979(4)$ Å, $c' = c = 8.7115(1)$ Å at 293K(20°C) with tetragonal ratio $c'/a' \sim 1.06$ [2].

Copper ferrite is a Néel collinear ferrimagnetic material with a ferromagnetic ordering of the magnetic moments of Fe^{3+} in the tetrahedral (A) and moments of Fe^{3+} and Cu^{2+} in the octahedral (B) positions with opposite directions of magnetization of the sublattices at temperatures up to $T_N\sim 750$ K. The magnetic moment in the A-positions (Fe^{3+}) and the total one in the B-positions ($Fe^{3+}Cu^{2+}$) at T< 30 K are equal to 4.06(6) and 4.89(8) μ_B, respectively

[5]. The difference between these values corresponds to the spin moment of Cu^{2+}. The magnetization can be easily assessed assuming magnetic moments of Fe^{3+} and Cu^{2+} ions to be close to 4.06 and 0.83 μ_B, respectively, and antiparallel orientation of octahedral and tetrahedral magnetic moments. Then, from (1), we have M_S=(0.83+6.46δ) μ_B per formula unit and migration of Cu^{2+} ions into tetrahedral site (i.e., increasing δ) leads to significant increase of the magnetic moment of samples.

Temperature dependence of Mössbauer spectra on ^{57}Fe nuclei in polycrystalline samples have been reported in [6]. The absorption area ratio of the ^{57}Fe nuclei in tetrahedral A-sites I_A to octahedral B-sites I_B can be written as:

$$\frac{I_A(T)}{I_B(T)} = \frac{(1-\delta) \cdot f_A(T)}{(1+\delta) \cdot f_B(T)} \tag{2}$$

where f_A and f_B is recoil-free fraction of the ^{57}Fe nuclei in tetrahedral A-sites and octahedral B-sites, respectively. The Debye model gives the following expression for the recoil-free fraction [7]:

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

where M is mass of ^{57}Fe nuclei, E_γ =14.4 keV is γ-ray energy of Mössbauer transition, k_B is Boltzmann factor, c is velocity of light, and Θ represents Debye temperature.

The Debye temperatures derived from the temperature dependence of the resonant absorption area of Mössbauer spectra at low temperatures in CuFe$_2$O$_4$ polycrystalline sample from Eq.(3) are Θ_A ~598 K and Θ_B ~285 K for tetrahedral and octahedral sites respectively[6].

2. Experimental details

The CuFe2O4 thin films were deposited at 50 or 200 W RF power on fused quartz substrates from the polycrystalline target, the details were published elsewhere [8-10]. The film thickness was between 90 and 280 nm. Several samples were studied in detail: along with as-deposited samples we measured samples annealed for 2 h in air at temperatures up to 850 °C and subsequently either slowly cooled (SC) to room temperature or quenched (Q) into liquid nitrogen; the characteristics of the samples are summarized in Table 1.

Tab. 1. *Thin films samples parameters, $4\pi M_S$ - magnetization; T_G - annealing temperature; Q - sample quenched to 80 K; SC - slowly cooled to room temperature; H_C – coercive field.*

Sample	Thickness [nm]	*RF* power[W]	T_G[°C]	$4\pi M_S$[G]	H_C[Oe]	Notes
Q	110	50	850	2300	500	Cubic, Q
SC50	280	50	850	1500	1250	Tetragonal, SC
SC200	230	200	850	1600	1450	Tetragonal, SC

The X-ray diffraction studies show that SC samples were tetragonal with ratio c'/a'=1.05 and Q samples were cubic, c'/a'= 1. The annealed samples deposited at 50 W RF power show strong (1 1 1) preferred orientation [10]. The as-deposited samples exhibited reduced magnetic moment because of large grain boundary volume. Magnetic moment increases with annealing temperature due to improving crystallinity of the films and increasing volume of the ferrite phase. The quenched samples exhibit higher moments compared to SC ones due to redistribution of Cu^{2+} ions between octahedral and tetrahedral sites [8, 9].

The Conversion Electron Mössbauer Spectroscopy (CEMS) experiments of $CuFe_2O_4$ samples were accomplished with a ^{57}Co/Rh source using a conventional constant acceleration spectrometer by Wissel. The velocities and isomer shifts (IS) are given relative to α-Fe at room temperature. All Mössbauer spectra of the thin film samples were evaluated using program CONFIT [11] .

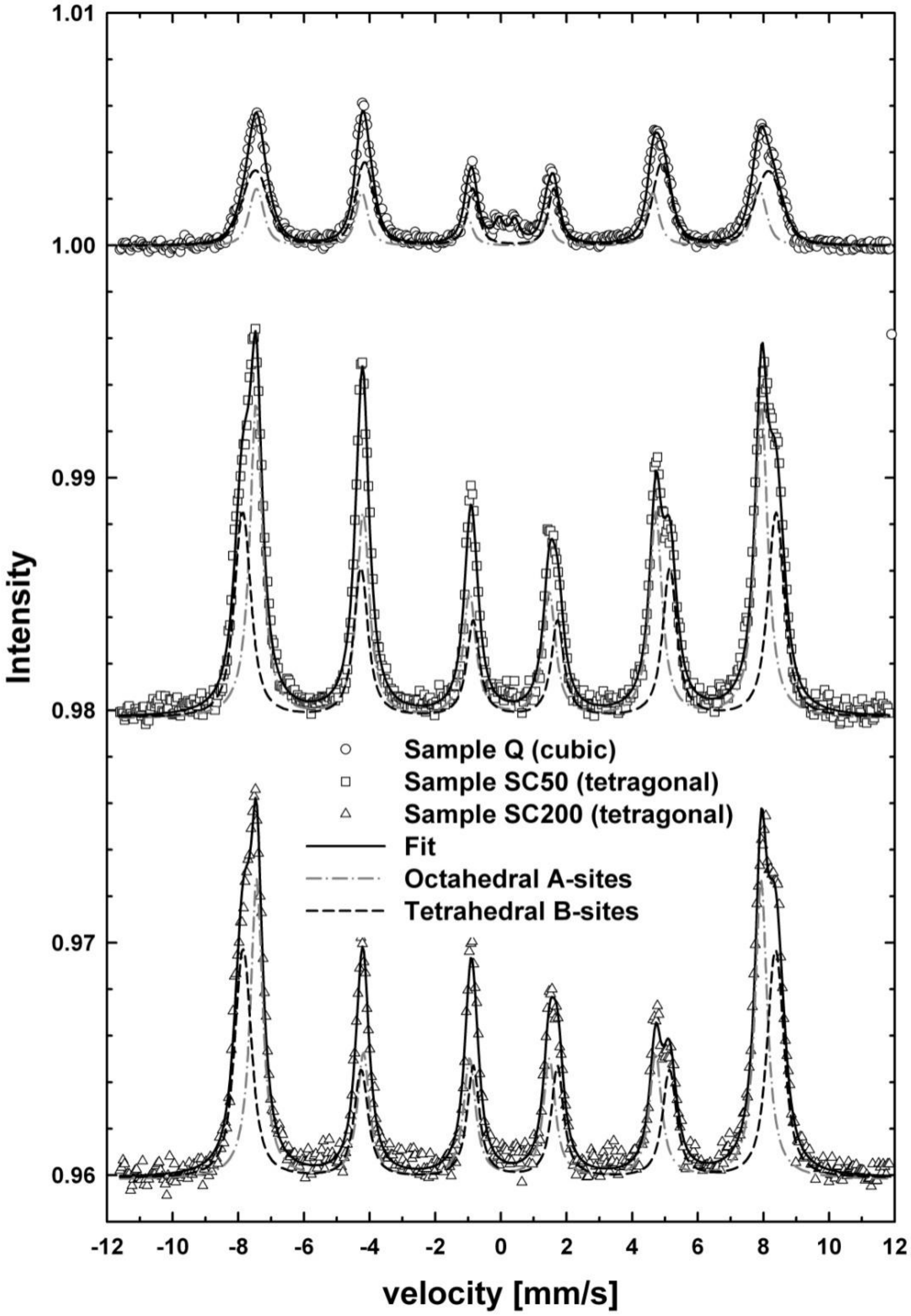

Fig. 1: *CEMS spectra at room temperature of $CuFe_2O_4$ thin films.*

3. Results and discussion

The conversion electron Mössbauer spectra of $CuFe_2O_4$ thin films at room temperature are illustrated in Fig. 1. The two sextets consist of wide lines and the best fit was obtained by using a hyperfine field distribution. The hyperfine parameters (isomer shift-*IS*, quadrupole shift-*QS* and average hyperfine magnetic field-B_{hf}) typical for $CuFe_2O_4$ obtained from these fits for tetragonal samples SC50 and SC200, see Tab. 2, are in good agreement with hyperfine parameters derived from nanorod and polycrystalline samples[6, 15]. Small amount of Cu^{2+} ions in in octahedral B-sites ($\delta \sim 0.1$) of tetragonal thin films correspond with values of $\delta \approx 0.05$-$0.1$from [2, 4]. The amount of Cu ions in tetrahedral sites was derived by means of two different procedures: first we assumed Θ_A ~598 K and Θ_B ~285 K from [6] and using Eqs. (2,3) arrived at $f_A/ f_B=1.60$ and designated the value δ^*. Alternately we used Eq.(2) and $I_A/ I_B=1.17$ from [12] and $\delta \sim 0.06$ from [2] which gave the value $f_A/ f_B=1.32$ and the fraction derived in this way is given as δ in Table 2.

Tab. 2. *Hyperfine parameters at room temperatures derived from CEMS spectra of thin films samples; IS – isomer shift; QS – quadrupole shift;* B_{hf} *– magnetic hyperfine field; I – intensity of spectra components.*

Sample	IS_A [mm/s]	IS_B [mm/s]	QS_A [mm/s]	QS_B [mm/s]	B_{hf}^A [T]	B_{hf}^B [T]	$I_{2,5}/ I_{3,4}$	I_A	I_B	I_A/ I_B	δ^*	δ
Q	0.21	0.36	0.02	-0.04	47.6	48.6	2.07	0.32	0.68	0.47	0.55	0.47
SC50	0.25	0.35	-0.02	-0.18	47.8	50.5	1.05	0.56	0.44	1.27	0.11	0.02
SC200	0.25	0.35	-0.02	-0.18	47.8	50.4	1.65	0.51	0.49	1.04	0.21	0.12

Freezing of cubic crystal structure in sample “Q” quenched into liquid nitrogen has an impact on hyperfine parameters, especially decreasing quadrupole shift QS_B and magnetic hyperfine field B_{hf}^B, which is caused by forcing Cu^{2+} ions out of the octahedral B-sites and thus cancelling the Jahn-Teller distortion of the octahedra. Cu concentration in tetrahedral sites increases in cubic Cu-ferrite to approximately $\delta \sim 0.5$. This is twice the value obtained from Faraday rotation and magnetic circular dichroism spectra of the same sample $\delta \sim 0.25$ [13, 14]. The quenched sample with the highest δ is cubic and displays the lowest anisotropy as seen from the magnitude of H_C from Tab. 1 and $I_{2,5}/ I_{3,4}$ from Tab. 2. The latter value may be interpreted as corresponding to the homogeneously random distribution of the directions of magnetization in the sample. The lower values of this ratio for SC samples indicate the tendency of magnetization to turn more from the in-plane orientation than corresponds to the random distribution.

4. Conclusions

The character of temperature changes in the structural parameters during the transition from cubic to tetragonal phase indicates that this transition is based on the migration of copper and iron atoms between the tetrahedral A and octahedral B sites in the spinel structure and the Jahn–Teller distortion arising from the octahedral cupric Cu^{2+} ions . Mössbauer spectroscopy use ^{57}Fe nuclei as a local probe is via hyperfine interactions, especially electric quadrupole and magnetic dipole interactions, sensitive to the distortion of crystal structure. The absorption area ratio I_A/ I_B of ^{57}Fe nuclei is sensitive to the concentration of Cu^{2+} ions in A- and B- sites of spinel structure and may give some estimate of the deviation of the cation distribution from the ideal inverse spinel with all Cu ions in B- sites.

The change of the symmetry from cubic to tetragonal is also expressed in higher magnetocrystalline anisotropy of the SC samples.

Acknowledgement

The authors are grateful to Professor S. Prasad for providing the samples for this research and thank the Czech Science Foundation for financial support (grant GA CR 16-04340S).

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