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Composition dependence of discontinuous magnetization in $Cu_xFe_{3-x}O_{4+\delta}$

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The spinel series $Cu_xFe_{3-x}O_{4+\delta, 0 \leqslant \delta \leqslant 0.4}$ (where $x = 0.2$, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) has been investigated by means of X-ray diffraction and Barkhausen jumps. Analysis of X-ray intensity data showed that this system separates into two phases at $x < 1$. The percentage of phase separation decreases with increasing copper content. The system shows a single phase at $x = 1$. The mean potential difference, V_B, and the frequency, F_B, of Barkhausen jumps were measured as a function of the magnetizing current. Addition of copper enhances the irreversible motion of domain walls. The sample with $x = 1$ shows the highest values of V_B and F_B. The potential energy of the walls increases with increasing copper content.

1. Introduction

The ferrimagnetic spinel $CuFe_2O_4$ exists in tetragonal and cubic forms depending on the method of preparation and the cooling conditions [1, 2]. This is attributed to the distribution of Cu^{2+} and Fe^{3+} ions among the two nonequivalent tetrahedral (A) and octahedral (B) sites. $CuFe_2O_4$ is an inverse ferrite, the Cu^{2+} ions occupying the octahedral sites [3, 4]. It was recognized by Néel [5] that, Cu^{2+} ions exist on both A- and B-sites in the spinel $CuFe_2O_4$. Several authors [6–8] have reported that a small fraction, y (not exceeding 0.2), of Cu^{2+} ions can occupy the A-sites. The cation distribution is expressed as

$$(Cu_y^{2+}Fe_{1-y}^{3+})_A[Cu_{1-y}^{2+}Fe_{1+y}^{3+}]_BO_4^{2-}$$

Barkhausen jumps (Bj) in ferrites are strongly dependent on the cation distribution between the A- and B-sites in the spinel structure [9–12]. Bj in ferri- and ferromagnetic materials arise when the material is cycled in an alternating field. The jumps are due to the irreversible motion of the magnetic domain walls [13]. The aim of the present work was to study the kinetics of formation of copper ferrite, due to the reaction

$$x\text{CuO} + (1.5\text{–}0.5x)\,\alpha\text{–Fe}_2\text{O}_3 \rightarrow \text{Cu}_x\text{Fe}_{3-x}\text{O}_{4+\delta} \quad (1)$$

by using X-ray diffraction technique and Barkhausen effect.

2. Experimental procedure

Polycrystalline samples of $Cu_xFe_{3-x}O_{4+\delta}$, $0 \leqslant \delta \leqslant 0.4$, (where $x = 0.2$, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0) were prepared by the standard ceramic method using analytical reagent-grade mixtures of CuO and α-Fe_2O_3 in powder form with appropriate ratios. They were well ground and presintered at 750 °C in air for 5 h soaking time, then compressed at constant pressure (3×10^8 Pa) to form pellets of 13 mm diameter and ~0.3–0.5 mm thick. The pellets were sintered at 1000 °C for 5 h and then slowly cooled to room temperature. Powder X-ray diffraction patterns were recorded using a Philips diffractometer with CuK_α ($\lambda = 0.1541$ nm) to characterize the samples.

An induction technique was used to measure the mean potential difference, V_B, and the frequency of cluster, F_B, of Bj as a function of the magnetizing current. The technical data of the magnetizing and pick-up coils and block diagram of the circuit used were given elsewhere [9, 14].

3. Results and discussion

3.1. X-ray analysis

All the samples of the present series of $Cu_xFe_{3-x}O_{4+\delta}$ have been investigated by X-ray diffraction technique at room temperature. The obtained diffraction patterns illustrate the main reflection planes of the spinel structure of ferrites. These planes are (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (5 1 1) and (4 4 0). The values of d-spacing for the recorded peaks of $Cu_xFe_{3-x}O_{4+\delta}$ were calculated according to Bragg's law. These values were in agreement with the JCPDS card of cubic $CuFe_2O_4$. The diffraction patterns of the samples with $x = 0.2$–0.8 showed, in addition to the above-mentioned planes, another six planes characterizing α-Fe_2O_3 (antiferromagnetic). These planes are (0 1 2), (1 0 4), (1 1 3), (0 2 4), (1 1 6) and (3 0 0). In the diffraction pattern of the samples with $x = 0.2$ and 0.3, the plane (1 0 4) of α-Fe_2O_3 represents 100% intensity, relative

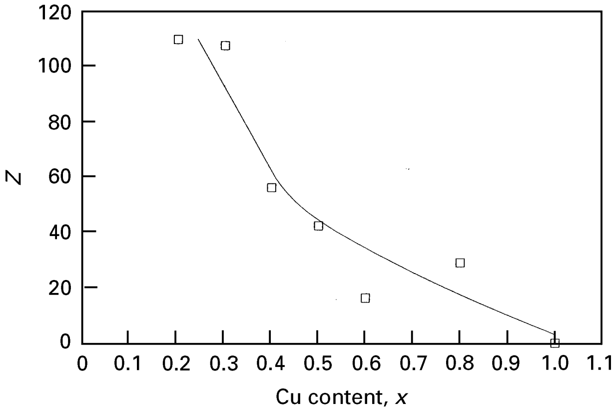


Figure 1 Change of the percentage of relative intensity $Z = I_{(1\,0\,4)\alpha-Fe_2O_3}/I_{(3\,1\,1)Cu_xFe_{3-x}O_{4+\delta}}$ with copper content.

TABLE I The change of the lattice parameter, a, with copper content.

x	0.2	0.3	0.4	0.5	0.6	0.8	1.0
$a \pm 0.001$ (nm)	0.832	0.836	0.836	0.833	0.841	0.835	0.837

to all recorded peaks. However, in the diffraction patterns of the samples with $x = 0.4$–1.0, the plane (3 1 1) of $CuFe_2O_4$ represents 100% intensity relative to all peaks. Generally the increase in copper content causes the decrease of the intensity of α-Fe_2O_3 planes, as well as the increase of the intensity of $CuFe_2O_4$ planes. Fig. 1 shows the percentage of the relative intensity $I_{(1\,0\,4)\alpha-Fe_2O_3}/I_{(3\,1\,1)Cu_xFe_{3-x}O_{4+\delta}}$, represented here as Z, with copper content. It is clear that Z decreases with the increasing copper content, indicating the increase in the percentage of ferrimagnetic copper ferrite as well as the decrease in the percentage of antiferromagnetic α-Fe_2O_3. At $x = 1.0$, all the peaks of α-Fe_2O_3 disappeared ($Z = 0$), and the pattern showed only the peaks of $CuFe_2O_4$, indicating the formation of single-phase $CuFe_2O_4$. The lattice parameters were calculated using the least square "LSQ" computer program. Table I shows the change of lattice parameter, a, with copper content.

The lattice parameter of cubic $CuFe_2O_4$ from the JCPDS card is 0.837 nm. It is in a good agreement with our sample of $x = 1.0$. The lattice parameters of the other samples are also in the same range.

3.2. Effect of copper content on F_B and V_B

Fig. 2 shows the change of V_B with the magnetizing current (50 Hz) for the series $Cu_xFe_{3-x}O_{4+\delta}$ (where $x = 0.2$, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0). The corresponding values of the magnetic field strength are given on the figure. The increase of copper content causes the increase of V_B over the whole range of the applied magnetizing field. Fig. 3 shows I–F_B curves for the above-mentioned series. These curves show the same behaviour as the I–V_B curves. The frequency of jumps,

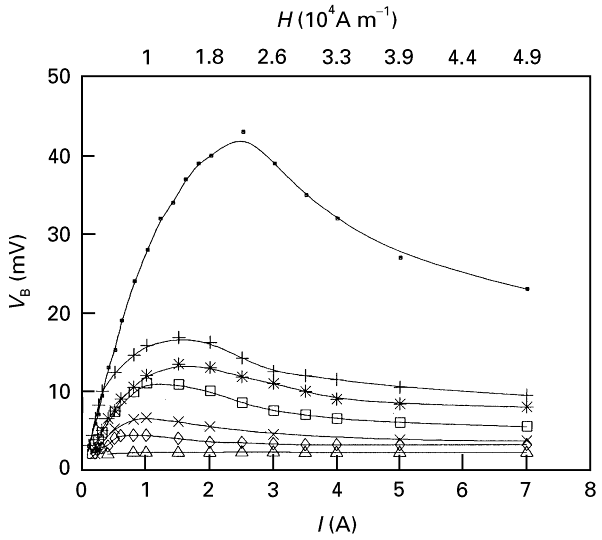


Figure 2 V_B as a function of the magnetizing current for $Cu_xFe_{3-x}O_{4+\delta}$. x: (●) 1.0, (+) 0.8, (∗) 0.6, (□) 0.5, (×) 0.4, (◇) 0.3, (△) 0.2.

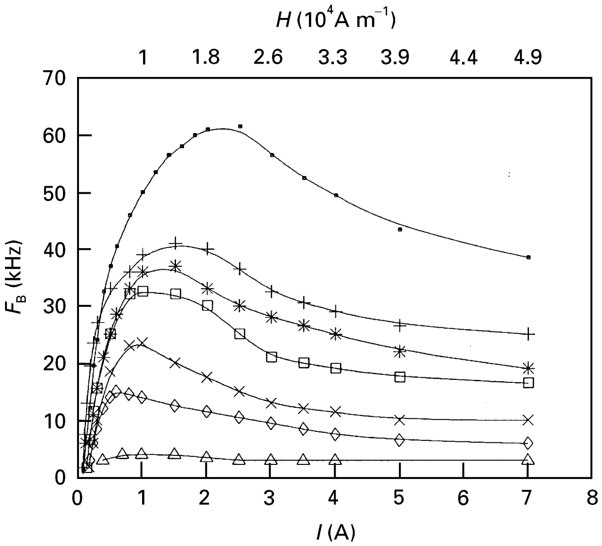


Figure 3 F_B as a function of the magnetizing current for $Cu_xFe_{3-x}O_{4+\delta}$. For key, see Fig. 2.

F_B, will be taken as a function of the number of jumps. The higher the value of F_B the larger is the number of jumps [9]. Fig. 4 shows the change of F_B and V_B, taken at constant magnetizing currents of 1.5, 2.5, 3.0 and 7.0 A, with copper content. It is clear that F_B and V_B increase with the increasing copper content. The increase of F_B and V_B takes place in two stages (I and II, as shown in Fig. 4). Stage I corresponds to a copper content up to $x = 0.8$. Stage II corresponds to a copper content of $x = 0.8$–1.0. In stage II, F_B and V_B increase abruptly in comparison to stage I. These results could be explained as follows. The cation distribution of $Cu_xFe_{3-x}O_{4+\delta}$ could be written as

$$(Cu_y^{2+}Fe_{1-0.5x-y}^{3+})_A[Cu_{x-y}^{2+}Fe_{2-0.5x+y}^{3+}]_BO_{4+\delta}^{2+} \qquad (0 \leqslant \delta \leqslant 0.4)$$

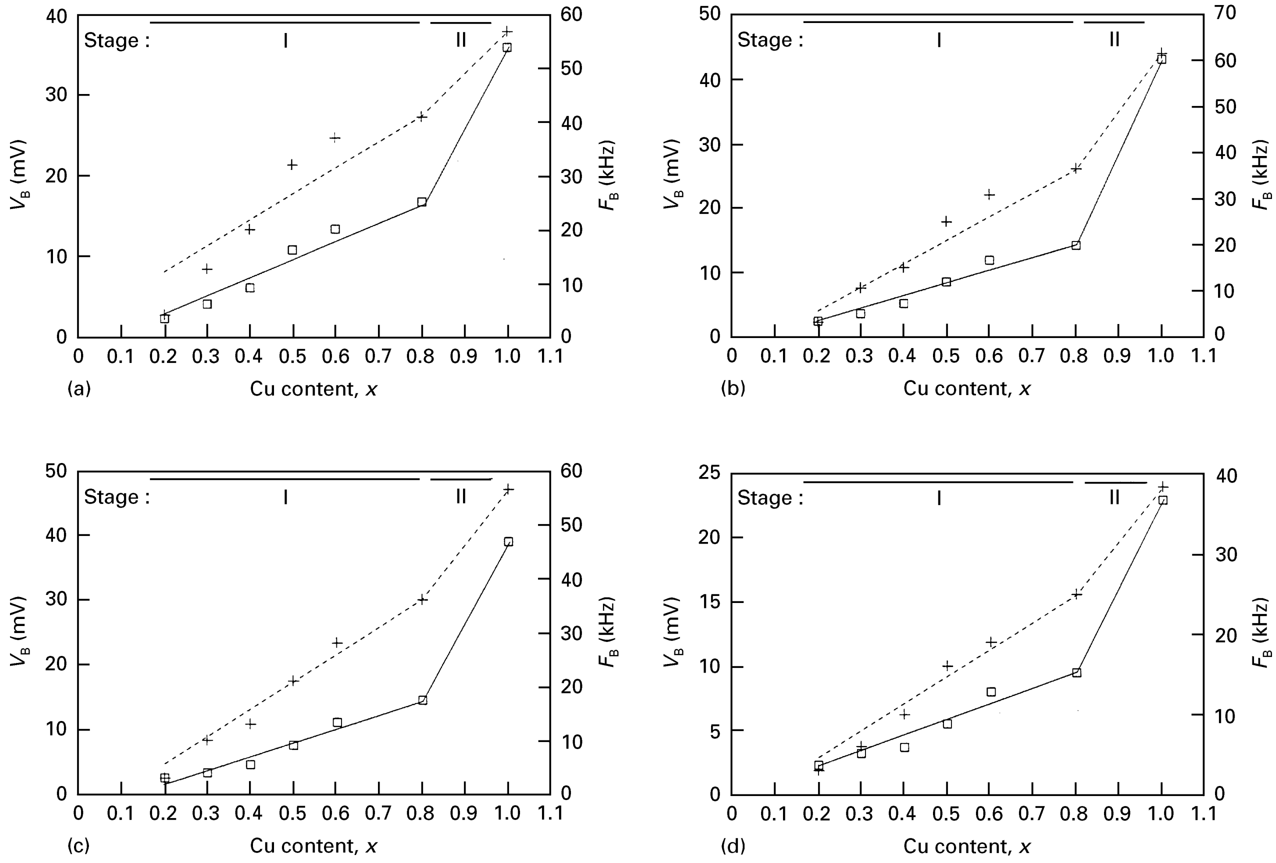
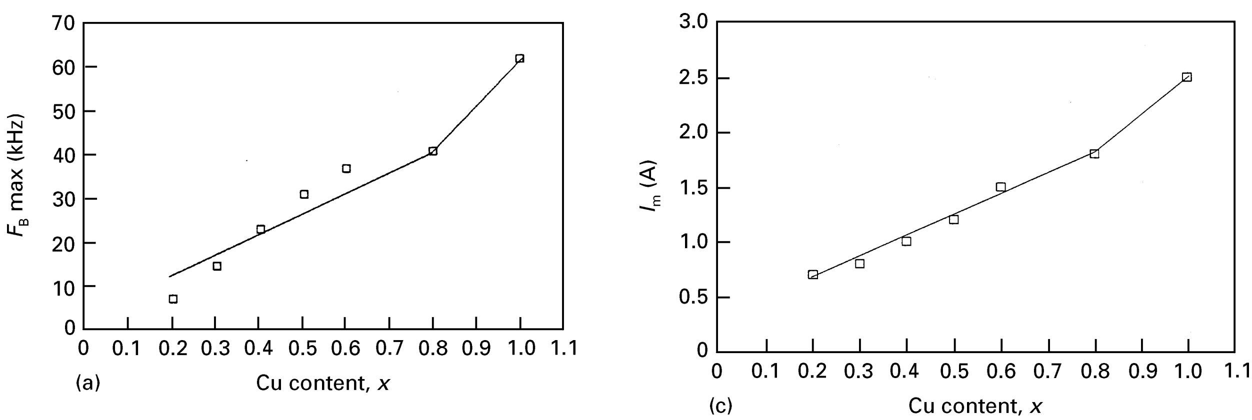


Figure 4 Dependence of (+) F_B and (□) V_B on copper content at constant magnetizing currents: (a) $I = 1.5$ A, (b) $I = 2.5$ A, (c) $I = 3$ A, (d) $I = 7$A.



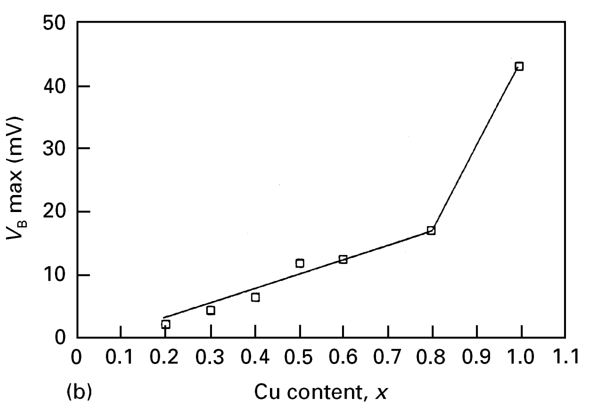


Figure 5 Dependence of F_B max, V_B max and I_m on copper content.

The Cu^{2+} ions occupy mainly the B-sites and a small fraction, y, of Cu^{2+} ions (magnetic moment = 1 Bohr magneton), not exceeding 20% when $x = 1.0$ ($CuFe_2O_4$), can occupy the A-sites [6–8]. An amount, y, of Fe^{3+} ions (magnetic moment = 5 Bohr magneton) will be forced to migrate from A- to B-sites. This would increase the net magnetic moment of the composition (increase of the ionic spins ordering). The number of the domain walls, as well as the percentage of ferrimagnetism, would increase causing the observed increment of F_B and V_B. At $x = 1.0$, the sample is 100% ferrimagnetic (complete disappearance of antiferromagnetic phase, $Z = 0$). The magnetic

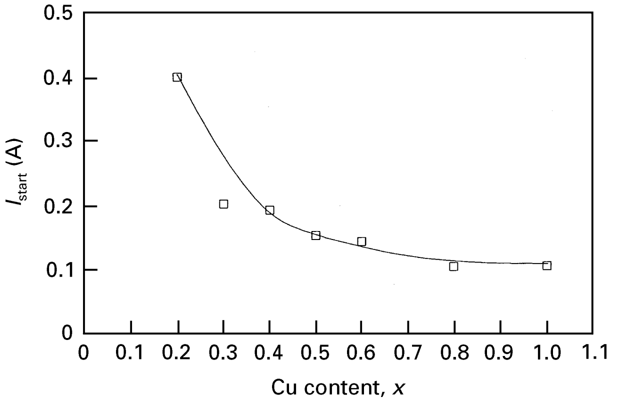


Figure 6 Dependence of I_{start} on copper content.

moment reaches its highest value (highest ionic spins ordering) relative to the other samples. This would cause a sharp increase in the number of mobile domain walls, giving rise to the observed abrupt increase of F_B and V_B in stage II.

Generally, F_B and V_B increase with the increase in the applied magnetizing current until maximum values of F_B and V_B are reached, then F_B and V_B begin to decrease with further increase of the magnetizing current (Figs 2 and 3). The maximum values of F_B and V_B are denoted here by $F_B$max (maximum number of jumps) and $V_B$max (maximum mean potential difference of jumps). For each individual value of copper content, these values take place at a certain magnetizing current, I_m. This corresponds to the magnetic pressure needed to force the maximum number of domain walls to participate in the irreversible motion. Figs 5a–c show the change of $F_B$max, $V_B$max and I_m with copper content. $F_B$max and $V_B$max (Fig. 5a and b) show the same behaviour of F_B and V_B as described previously in Fig. 4, indicating the increase in the percentage of ferrimagnetism and magnetic moment with increasing copper content.

The random potential energy diagram of the domain walls describes the wall-defect interaction [4]. It consists of many humps of different heights and slopes representing the different pinning sites inside the material. The increase in the magnetic field (magnetic pressure exerted on the walls) causes many walls to climb many different humps. At a critical value of magnetic pressure, some walls jump to next humps giving rise to Bj. The increase in I_m with increasing copper content, Fig. 5c, indicates that the magnetic pressure needed to force the maximum number of walls to participate in the irreversible motion increases with increasing copper content. The humps would be of higher number, heights and slopes. This indicates the increase in the potential energy of the walls with increasing copper content.

Copper content also has a considerable effect on the value of the magnetizing current, I_{start}, at which V_B starts to appear. Fig. 6 shows that I_{start} decreases with increasing copper content. This could be explained by the sample of $CuFe_2O_4$ representing the case of relatively 100% ferrimagnetism and highest magnetic moment. Thus, it would be the sample of the highest permeability in comparison to the other samples. Accordingly Bj appears at the lowest magnetizing field.

4. Conclusions

1. The increasing copper content causes a decrease in the intensity of α-Fe_2O_3 planes as well as an increase in the intensity of $CuFe_2O_4$ planes.
2. Addition of copper enhances the irreversible magnetization, which indicates an increase of magnetic ordering and magnetic moment.
3. The magnetic pressure needed to force the maximum number of walls to participate in the irreversible motion increases with increasing copper content. This indicates an increase in the potential energy of the walls with increasing copper content.

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