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The Influence of Ni^{2+} Ions on the Distribution of Mg^{2+} and Cu^{2+} Ions in Spinel Ferrites

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Cation distribution in quenched and furnace-cooled samples of composition $Ni_xM_{1-x}Fe_2O_4$ (where M is either Mg^{2+} or Cu^{2+}) has been studied through magnetization measurements. It has been found that cation distribution in these mixed ferrites cannot be predicted by site preference energies. In magnesium–nickel ferrites, cation distribution is controlled by heat treatment up to $x = 0.5$, beyond which the effect of heat treatment diminishes. Addition of Ni^{2+} ions in copper ferrite reduces the diffusibility of Cu^{2+} ions and the distribution tends toward inverse spinel in the high-nickel region.

1. Introduction

The properties of spinel ferrites depend on cation distribution that may be suitably modified by (a) addition of impurity cations and (b) controlling the preparative conditions, particularly the heat treatment. The compounds magnesium ferrite and copper ferrite are partly inverse spinels and the cation distribution in them is strongly dependent on the factors mentioned because of the high diffusibility of the Mg^{2+} and Cu^{2+} ions. The distribution of these ions in the spinel lattice as a function of temperature is expressed as (*1*):

$$\frac{x\,(1 + x)}{(1 - x)^2} = \exp(-E/RT), \qquad (1)$$

where x is the fraction of the Mg^{2+} (or Cu^{2+}) occupying the A sites and E is the energy of activation necessary to interchange a B-site Fe^{3+} ion with an A-site Mg^{2+} (or Cu^{2+}) ion. Ni^{2+} ions, on the other hand, occupy only the octahedral sites due to their stronger site preference. The aim of the present investigation is to understand the effects of Ni^{2+} ions as well as that of heat treatment on the distribution of Mg^{2+} and Cu^{2+} ions in the two partly inverse spinel ferrites, $MgFe_2O_4$ and $CuFe_2O_4$. It should be noted, however, that the cation distribution in the furnace-cooled samples is only useful for comparison as it does not represent the equilibrium distribution at a given temperature.

2. Experimental

The following compositions $Ni_xM_{1-x}Fe_2O_4$ (where M is Mg^{2+} or Cu^{2+} and x varies from 0 to 1) were prepared by mixing the requisite quantities of high-purity NiO, α-Fe_2O_3 and MgO (or CuO) for several hours adding acetone, pelletizing the dried mixture into disks of 16 mm diameter and 5 mm thickness and firing by gradually raising the temperature. The compounds $Ni_xMg_{1-x}Fe_2O_4$ were sintered

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at 1573 K for 3 hr, and the compositions $Ni_xCu_{1-x}Fe_2O_4$ at 1323 K for 24 hr. In each case, one set of samples was quenched from the sintering temperature to room temperature by dropping the pellets into water or liquid nitrogen and another set was cooled in the furnace at the rate of 60°/hr by adjusting the furnace. All these operations were carried out in air.

The X-ray powder patterns were recorded using Co$K\alpha$ radiation on a Philips (PW 1010) X-ray diffractometer. Magnetization measurements at various temperatures were carried out on a hysteresis loop tracer (*2*).

3. Results and Discussion

The X-ray diffraction patterns showed that all the compositions were monophasic spinels. All the compositions were found to be cubic except annealed $CuFe_2O_4$ and $Ni_{0.2}Cu_{0.8}Fe_2O_4$, which were tetragonal.

The cation distribution in these compounds have been calculated from saturation magnetization at 0 K (σ_0) obtained by extrapolating the saturation magnetization (σ_s) vs temperature plots (*3*, *4*). The following assumptions were made in calculating the cation distributions:

(a) The arrangement of spins in these systems are collinear; i.e., there is no canting (*5*);

(b) Ni^{2+} ions occupy only the B sites; this is justified as the other ions (Mg^{2+}, Cu^{2+} and Fe^{3+}) have much lower octahedral-site preference (*6*);

(c) Iron is present only as Fe^{3+}. This is supported by the high resistivity of these samples (~10^7 ohm-cm at 300 K) (*3*) and Mössbauer isomer shifts (0.3–0.8 mm/sec with respect to iron) indicating the presence of iron in trivalent state only (*7*);
and

(d) Cu^{1+} ions cannot be present in the furnace-cooled samples of nickel–copper ferrites because the prolonged heat treatment in air should oxidize any Cu^{1+} ions present.

The cation distribution, therefore, can be written as

$$M^{2+}_{a(1-x)}Fe^{3+}_{1-a(1-x)}[Ni^{2+}_x M^{2+}_{(1-a)(1-x)} Fe^{3+}_{1+a(1-x)}]O^{2-}_4, \quad (2)$$

where

$$a = \frac{n_B - x\mu_{Ni^{2+}} - (1-x)\,\mu_{M^{2+}}}{2(1-x)[\mu_{Fe^{3+}} - \mu_{M^{2+}}]}. \quad (3)$$

The values for $\mu_{Ni^{2+}}$, $\mu_{Fe^{3+}}$, $\mu_{Cu^{2+}}$ and $\mu_{Mg^{2+}}$ were taken as 2.3, 5.0, 1.0, and 0.0 Bohr magnetons, respectively. n_B is the experimentally determined saturated magnetic moment at 0 K, calculated according to (*8*):

$$n_B = \frac{\sigma_0 \text{ molecular weight}}{5585}. \quad (4)$$

The n_B values and y, the percentage of M^{2+} ions in an A site

$$\left(y = \frac{M^{2+}_{\text{A site}} \times 100}{M^{2+}_{\text{Total}}}\right)$$

for the quenched and furnace-cooled samples of various compositions, are given in Table I. The effectiveness of quenching is ensured by the fact that the same value of magnetic moment was observed irrespective of whether the samples were quenched in water or liquid nitrogen. It is to be noted from Table I that although the uncertainty in the n_B value is small ($\pm 0.02\mu_B$) and constant, the errors in a values, because of its inverse dependence on $(1 - x)$, increase with x. However, in all the cases, except for copper–nickel ferrite with $x = 0.8$, the error is less than 8%. For the last-mentioned sample, the value of a for both quenched and furnace-cooled samples is small and comparable to the error.

It may noted from Fig. 1 that for $x < 1$, the percentage of Mg^{2+} or Cu^{2+} ions in the A sites is higher in case of quenched samples than the corresponding furnace-cooled

TABLE I

EFFECTIVE MAGNETIC MOMENTS AND CATION DISTRIBUTION PARAMETER y FOR THE FURNACE-COOLED AND QUENCHED FERRITES OF VARIOUS COMPOSITIONS

Composition x	$Ni_xMg_{1-x}Fe_2O_4$				$Ni_xCu_{1-x}Fe_2O_4$			
	Furnace-cooled		Quenched		Furnace-cooled		Quenched	
	n_B (μ_B)	y	n_B (μ_B)	y	n_B (μ_B)	y	n_B (μ_B)	y
0.0	1.20	12.0 ± 0.21	2.25	22.5 ± 0.21	1.39	4.9 ± 0.26	2.21	15.1 ± 0.26
0.2	1.18	9.0 ± 0.26	2.36	23.8 ± 0.26	1.66	6.3 ± 0.30	2.30	16.3 ± 0.30
0.4	1.39	7.8 ± 0.35	2.51	26.5 ± 0.35	1.98	9.5 ± 0.43	2.26	15.5 ± 0.43
0.5	1.49	6.8 ± 0.42	2.29	22.8 ± 0.42	1.99	8.5 ± 0.50	2.22	14.1 ± 0.50
0.6	1.73	8.8 ± 0.53	2.38	25.0 ± 0.53	2.03	7.9 ± 0.63	2.18	12.5 ± 0.63
0.8	2.19	17.5 ± 1.05	2.44	30.0 ± 1.05	2.07	1.6 ± 1.31	2.11	4.2 ± 1.31
1.0	2.30	—	2.30	—	2.30	—	2.30	—

Note. n_B values at 0 K (extrapolated) accurate to $\pm 0.02\ \mu_B$; y = percentage of M^{2+} ions on the A site.

samples. This results from the high diffusibility of these ions at high temperature.

Within each system, however, the experimentally determined cation distributions do not follow the trend expected from the known octahedral-site preference energy values (P) for these ions ($P_{Fe^{3+}} = -13.3$; $P_{Ni^{2+}} = +9.0$; $P_{Cu^{2+}} = -0.1$, and $P_{Mg^{2+}} = -5.0$ kcal/mole) (*9, 10*). Further, the behavior of Mg^{2+} and Cu^{2+} toward Ni^{2+} substitution are not analogous (Fig. 1).

In the Mg-Ni ferrites, the percentage of Mg^{2+} ions occupying the A sites decreases with increasing Ni^{2+} concentration (up to $x = 0.5$) showing that Ni^{2+} preferentially displaces Fe^{3+} ions rather than the Mg^{2+} ions. This is in agreement with what is expected. But beyond $x = 0.5$, the trend is reversed; i.e., the fraction of Mg^{2+} ions on A sites increases.

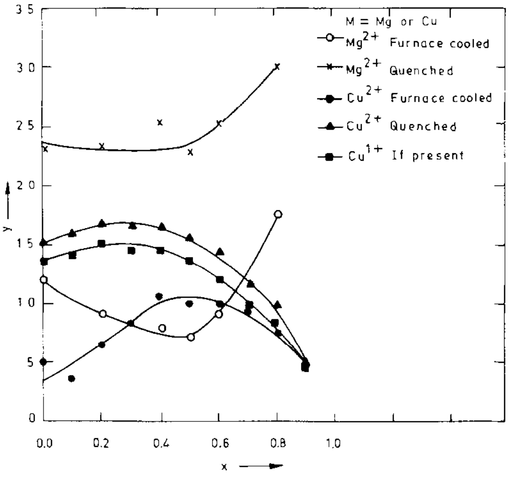

FIG. 1. Variation of y with composition for the system $Ni_xM_{1-x}Fe_2O_4$.

In the Cu–Ni ferriters with $x < 0.5$, substitution by Ni^{2+} ions displaces Cu^{2+} ions to the A sites which is contrary to the expected behavior. Above $x = 0.5$, the percentage of Cu^{2+} ions on the A sites gradually decreases.

We do not question the cation distribution calculated in these compounds, as in the majority of the cases it has been independently verified by Mössbauer spectroscopy [11] and ferromagnetic resonance studies [5]. It thus seems that the prediction of cation distribution in these ferrites based on site preference energy is not always possible. This conclusion is supported by the results of Robbins and D'Arey [10], whose studies on some oxide spinels have shown that the octahedral site preference of cations are not single-ion properties, i.e., the behavior of a particular ion toward another is influenced by the presence of a third ion.

In order to clearly visualise the competitive effects of Ni^{2+} substitution and heat treatment, the ratio $\delta = M_{\mathrm{A\,site}}$ (quenched sample)/$M_{\mathrm{A\,site}}$ (furnace-cooled sample) is plotted against x in Fig. 2. In the case of Mg–Ni ferrites with $x < 0.5$, it is evident that the cation distribution is predominantly controlled by heat treatment. If the cation distribution is to be controlled by the incorporation of Ni^{2+} ions, one would have obtained a near-constant value of δ. Beyond $x = 0.5$ in this system, there is a sharp decrease indicating a reduction of the effect of heat treatment.

For the Cu–Ni ferrites, δ decreases rather rapidly with increasing x up to 0.4. Thus, addition of Ni^{2+} seems to reduce the diffusibility of the Cu^{2+} ions in the lattice. Beyond $x = 0.4$, δ is nearly constant, showing that cation distribution has very little dependence on heat treatment in these compositions. The deviation of the δ vs x curve at $x = 0.8$ is spurious and is due to the fairly large error involved in the calculation of a for this sample that has already been mentioned.

In the case of Cu–Ni ferrites, the presence of Cu^{+} ions cannot be ruled out in the quenched samples. If such ions are formed in the quenched samples, they would occupy the A sites. Even if one assumes that all the copper ions present on A sites are monovalent, calculations show that the trend in the y vs x curve remains unchanged (Fig. 1), although the absolute value of y is reduced a little, showing that the uncertainty in the value of y due to the presence of monovalent copper is not large.

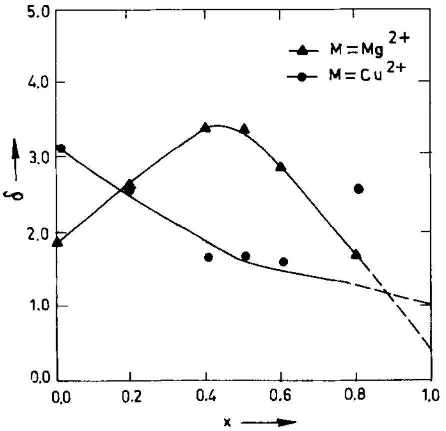

FIG. 2. Variation of the parameter δ with composition for the system $Ni_xM_{1-x}Fe_2O_4$.

4. Conclusions

The present study has shown that:

(a) The cation distribution in the magnesium–nickel and copper–nickel ferrites cannot be predicted on the basis of the octahedral-site preference energies;

(b) The distribution of Mg^{2+} ions on the magnesium–nickel ferrites is controlled by heat treatment for $x < 0.5$, beyond which the effect of heat treatment decreases;

(c) Cu^{2+} ions in the copper–nickel ferrites appear to become less diffusible as Ni^{2+} ions are introduced. The effect of heat treatment thus decreases with Ni^{2+} ions and the compositions tend toward an inverse distribution as prevalent in pure nickel ferrite, irrespective of heat treatment.

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