MAGNETIC PROPERTIES OF ZINC DOPED FERRITES

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A series of samples of the system $Co_{1-x}Zn_xFe_2O_4$ (x = 0.0, 0.3, 0.4, 0.5 and 0.8) have been prepared by the usual ceramic technique. X-ray analysis shows that they are cubic spinel (single phase). The lattice parameter a and the bulk density D are measured for the samples. The substitution experiments replacing Co^{2+} by Zn^{2+} furnish new significant fact concerning the magnetic behaviour of ferrites. The magnetic strength of the magnetic ions on the B- and A-sites can be varried relative to each other by the substitution of Zn^{2+}. The increase of density of the composition increases the magnetic interaction of the dipole moment at the B-sites.

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1. Introduction

An insight into the magnetic behaviour of the ferrites can be gained by performing certain substitutions for the ferric ion. Michel and Pouillard [1] substituted Al^{3+} for Fe^{3+} in Fe_3O_4, and they found that both the Curie temperature and size of the unit cell decreased linearly with the amount of aluminium added until a point was reached where approximately one ion out of seven Fe^{3+} was replaced by one Al^{3+}; beyond this point, both the Curie temperature and size of unit cell remained constant. They concluded from this work that only a limited amount of aluminium can be held in solid solution with Fe_3O_4.

Thermomagnetic investigations of promoted, unreduced iron oxide catalysts were carried out by Maxwell, Smart, and Brunauer [2] on Fe_3O_4 containing up to about 35 mole percent of Al_2O_3. The Curie temperature remained constant with

a reduction in the intensity of magnetization roughly proportional to the volume occupied by the Fe_3O_4 which indicated that the Al_2O_3 existed either as a separate phase or possibly in combination with FeO to form a ferrous aluminate.

Guillaud and Michel [3] have found a linear decrease in the saturation magnetic moment for magnetite with aluminium substituted until there was approximately 0.20 of an aluminium ion per molecule, presumably in solid solution. Although the authors state that their data is in agreement with the Néel theory [4], the way in which this agreement is established is not clear because of the lack of sufficient information as to the distribution of the magnetic ions in the lattice.

The replacement of trivalent iron in Fe_3O_4 is complicated by the fact that the iron ion can go from the ferrous to ferric state rather easily by a simple transfer of an electron. It, therefore, is desirable to perform substitution experiments with a material having more stable divalent ion.

Zn^{2+} ions prefer to occupy tetrahedral sites in the spinel lattice and in the mixed Co–Zn ferrites [5], the molecular formula is

$$Zn_x^{2+}Fe^{3+}\left[Co_{1-x}^{2+}Fe^{3+}\right]O_4.$$
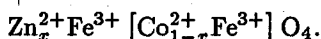
During sintering some of Fe^{3+} changes to Fe^{2+}, the electronic conductivity occurs due to exchange of electrons between trivalent and divalent iron ions Fe^{3+} and Fe^{2+}, respectively.

The aim of the present work is to study the effect of Zn additions on the lattice parameter, the density and the magnetic properties of $CoFe_2O_4$ ferrites.

2. Experimental.

2.1. Sample preparation

Samples of the system $Co_{1-x}Zn_xFe_2O_4$ ($x = 0.0$, 0.3, 0.4, 0.5 and 0.8) were prepared using the usual ceramic technique. The pure oxides were mixed and then ground to a very fine powder using an agate mortar made of carborundum. The samples in form of discs were sintered at 1200°C for two hours and slowly cooled to room temperature. The samples were polished to have uniform parallel surfaces. For magnetic measurements contacts on the sample surface were made by silver paste.

2.2. Lattice parameter and density measurements

The X-ray diffraction pattern for each sample was recorded by using a Shimadzu X-ray diffractometer (Model X D–3). The powder specimens were exposed to CuK_α radiation. The lattice parameter a was calculated from the X-ray diffraction pattern [5]. The bulk density D is determined by using the Archimedes principle in toluene according to the following equation:

$$D = \frac{W_s}{W_t}\rho_t,$$

where W_s denotes the weight of the specimen in air, W_t the apparent weight loss in toluene, and ρ_t the density of toluene.

The magnetic susceptibility was measured using susceptibility bridge, part of Molspin Minispin designed by L. Molyneux.

3. Results and discussion

3.1. Effect of Zn addition on the magnetic susceptibility and magnetization of $CoFe_2O_4$ ferrites

Figures 1 and 2 present graphs of magnetic susceptibility (χ) and the magnetization (M) as functions of x.

The increase of χ and M with Zn addition x is discussed as follows. The mixed cobalt–zinc ferrites have the formula $Zn_x''Fe_{1-x}'''(Me_{1-x}'Fe_{1+x}''')O_4$ with Me as the magnetic ion Co^{2+}; Zn^{2+} is known to have a preferential occupations for the tetrahedral A-sites. The presence of cobalt on the octahedral sites of the spinel
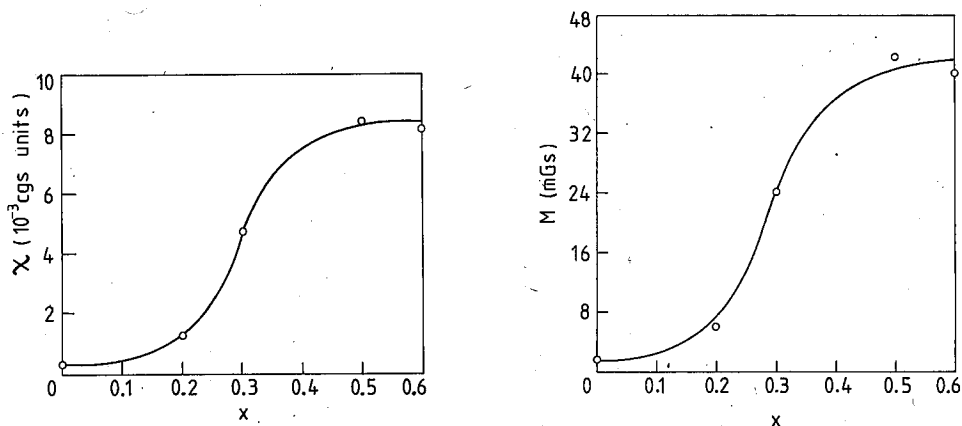

Fig. 1.   Variation of magnetic susceptibility χ with the zinc addition x.

Fig. 2.   Variation of magnetization M with the zinc addition x.

favours a conduction mechanism $Co^{2+} + Fe^{3+} \rightleftharpoons Co^{3+} + Fe^{2+}$ which explains the predominant conduction mechanism in $CoZnFe_2O_4$. The substituting zinc ions instead of cobalt ions in the composition.

Cobalt ferrite ($CoFe_2O_4$) has the inverse spinel structure in which the tetrahedral sites are occupied by Fe^{3+} and the octahedral sites are occupied half by Fe^{3+} and half by Co^{2+}. The excess cobalt or iron occupies the tetrahedral sites as Co^{3+} or Fe^{2+} [6] then generates holes or electrons as

$$Co^{3+} \rightarrow Co^{2+} + h^+,$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-.$$

The increase of Zn addition caused the movement of Fe^{3+} ions from the tetrahedral to octahedral sites. This should means an initial increase in the resultant magnetization on the B-sites.

3.2. Magnetization dependence on lattice parameter a

The lattice parameter of $CoFe_2O_4$ is determined to be 0.8385 nm, which is compared favourably with the value of 0.8394 nm [5]. The variation of lattice parameter a as a function of zinc addition x in $Co_{1-x}Zn_xFe_2O_4$ is previously represented. It showed that the lattice parameter increase linearly with the increase of zinc content.

The X-ray studies showed that the materials were in all cases homogeneous having the spinel structure.

We have for the magnetizations M_A and M_B of the A- and B-lattice sites, respectively, for N magnetic ions (only one kind) [4]:

$$M_A = \lambda Ng\beta SB_s(g\beta SH_A/kT),$$
$$M_B = \mu Ng\beta SB_s(g\beta SH_B/kT), \qquad (1)$$

where λ and μ are the fraction of magnetic ions on the A- and B-sites, respectively; H_A and H_B are the effective field acting on the magnetic ions in the A- and B-sites, respectively, which are expressed in terms of the molecular field coefficients (γ's) as

$$H_A = H_0 + \gamma_{AA}M_A - \gamma_{AB}M_B,$$
$$H_B = H_0 - \gamma_{AB}M_A + \gamma_{BB}M_B, \qquad (2)$$

where γ_{ij} is the Weiss molecular field coefficient for the interaction between the ions on the i_{th} and j_{th} sites, $B_s(\ )$ is the Brillouin function.

In the ferrimagnetic case we obtain the spontaneous magnetization ($H_0 = 0$) from Eqs. (1) and (2) in terms of the specific magnetization $\mathcal{Y}_A$ and $\mathcal{Y}_B$, given in terms of the number of Bohr magnetons per molecule as

$$\mathcal{Y}_A = B_s\left[(\tau/T)(\lambda\gamma_{AA}\mathcal{Y}_A - \mu\gamma_{AB}\mathcal{Y}_B)\right]$$
$$\mathcal{Y}_B = B_s\left[(\tau/T)(-\lambda\gamma_{AB}\mathcal{Y}_A + \mu\gamma_{BB}\mathcal{Y}_B)\right], \qquad (3)$$

where $\tau = Ng^2\beta^2s^2/k$, with

$$\mathcal{Y}_A = M_A/\lambda Ng\beta s, \quad \mathcal{Y}_B = N_B/\mu Ng\beta S.$$

The net specific magntization $\mathcal{Y}$ is given by

$$\mathcal{Y} = |\lambda\mathcal{Y}_A + \mu\mathcal{Y}_B|. \qquad (4)$$

From this theory Néel has calculated $\mathcal{Y}$ as a function of the temperature and arranged the curves into various types according to their shapes. The classification is made in terms of the parameters α and β which are defined as follows:

$$\alpha = \gamma_{AA}/|\gamma_{AB}|, \quad \beta = \gamma_{BB}/|\gamma_{AB}|.$$

The α's and β's give the strength and sign of the AA and BB interactions, respectively, in terms of the AB interaction.

In the present case, instead of one type of magnetic ion, as developed by Néel, we have two of them which can occupy either or both the A- or B-sites; and, furthermore, one cannot assume that the g factor for a given magnetic ion will be the same in both the A- and B-sites. This imposes mathematical complexities,
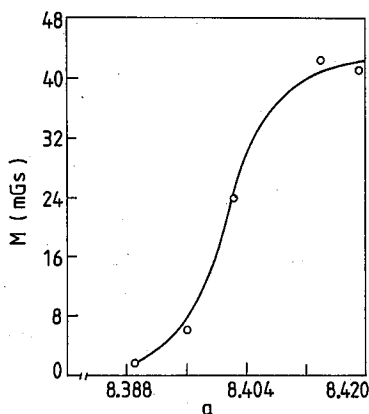
Fig. 3.   Variation of magnetization M with the lattice parameter a.
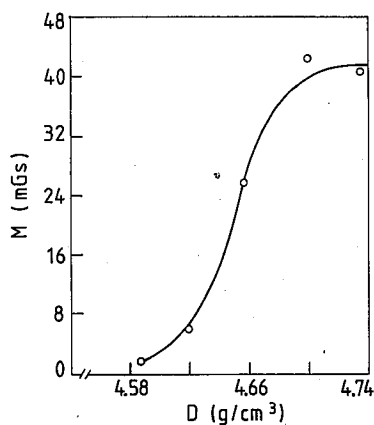
Fig. 4.   Variation of magnetization M with the bulk density D.

for Eqs. (1) through (4) would have to be modified accordingly before a detailed comparison with the theory could be accomplished. However, certain qualitative conclusions can be made.

For greater amounts of zinc and increase of the crystal size (Fig. 3), the magnetization from the B-sites predominates and the coupling weakens at the A-sites.

In conclusion, the $Co_{1-x}Zn_xFe_2O_4$ system can be prepared with a systematic linear variation in size of the unit cell which caused the magnetic strength of the magnetic ions on the A- and B-sites to vary relative to each other by the substitution of Zn^{2+} with a situation arising in the case of cobalt–zinc ferrite, where the magnetization on the B- and A-sites is not equal and opposite.

3.3. Effect of density on the magnetization of $Co_{1-x}Zn_xFe_2O_4$ ferrites

The effect of density on the magnetization (M) and the magnetic suscepti-bility (χ) of $Co_{1-x}Zn_xFe_2O_4$ are shown in Figs. 4 and 5. The increase of M and χ
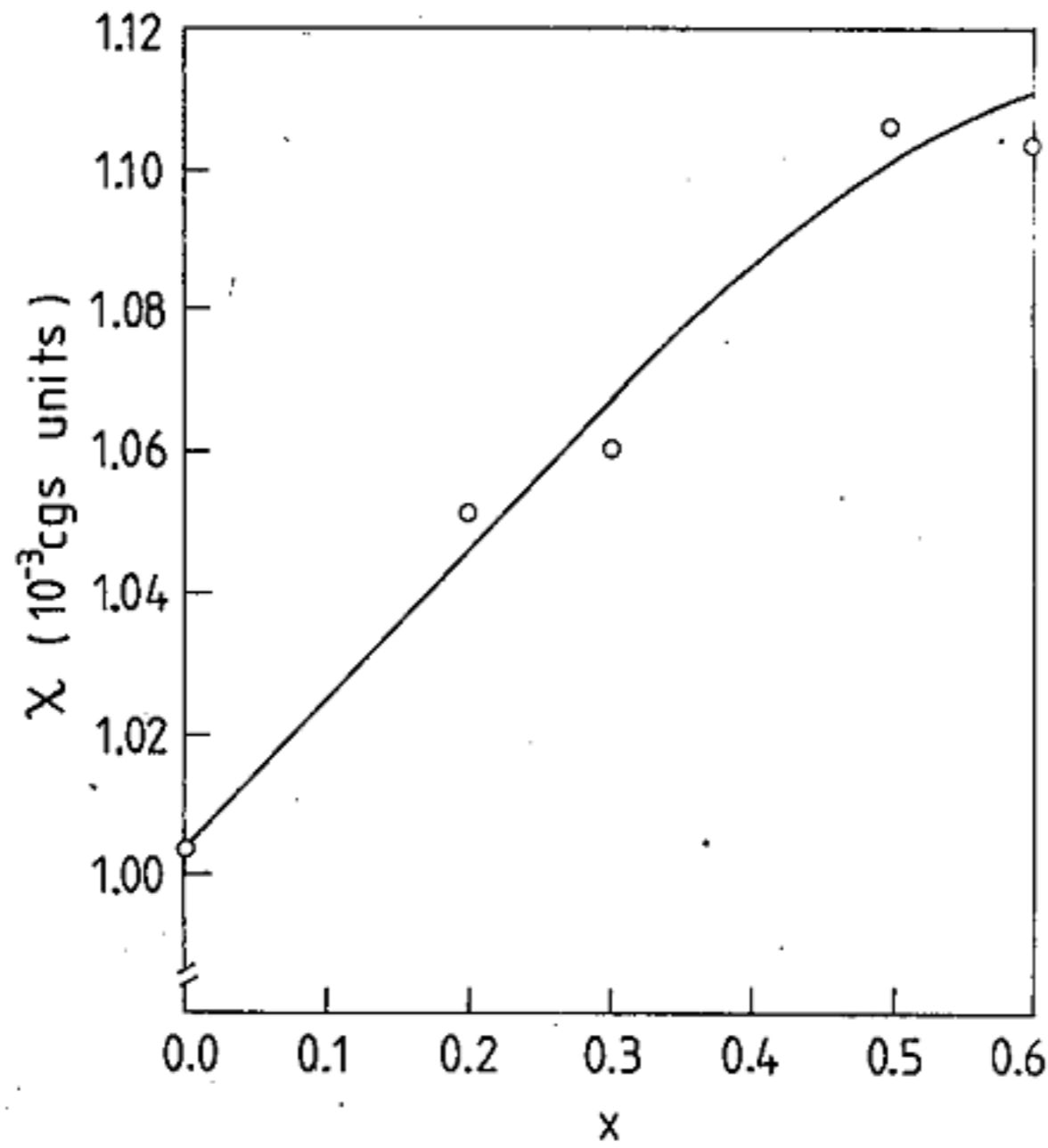

Fig. 5.   Variation of magnetic susceptibility χ with the addition of Zn x.

with density is due to the following: The increase of density reduced the porosity of the composition giving rise to the increase of the magnetic interaction at the B-sites. This interaction increases M with increasing density.

Acknowledgement

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