



On the magnetic properties of ultra-fine zinc ferrites

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Abstract

Zinc ferrite belongs to the class of normal spinels where it is assumed to have a cation distribution of $\text{Zn}^{2+}(\text{Fe}^{3+})_2(\text{O}^{2-})_4$, and it is purported to be showing zero net magnetisation. However, there have been recent reports suggesting that zinc ferrite exhibits anomaly in its magnetisation. Zinc ferrite samples have been prepared by two different routes and have been analysed using low energy ion scattering, Mössbauer spectroscopy and magnetic measurements. The results indicate that zinc occupies octahedral sites, contrary to the earlier belief that zinc occupies only the tetrahedral sites in a normal spinel. The amount of zinc on the B site increases with decrease in particle size. The LEIS results together with the Mössbauer results and the magnetic measurements lead to the conclusion that zinc occupies the B site and the magnetisation exhibited by ultrafine particles of zinc is due to short range ordering. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Spinel ferrites are commercially important materials because of their excellent electrical and magnetic properties [1]. These class of materials have been the subject of extensive studies by physicists and chemists alike. A whole range of distribution of cations is possible in spinels which can be represented generally by the formula

$(\text{Me}^{\text{II}})_\delta(\text{Fe}^{\text{III}})_{1-\delta}[(\text{Me}^{\text{II}})_{1-\delta}(\text{Fe}^{\text{III}})_{1+\delta}]\text{O}_4$ where the ions inside the brackets are said to occupy octahedral sites (B) and the ions outside the bracket occupy the tetrahedral sites (A) [2]. In the above formula when $\delta = 1$, it is called normal spinel. When $\delta = 0$ it is called an inverse spinel. When $\delta = \frac{1}{2}$ it is called random spinel. From the fundamental point of view, these materials serve as ideal candidates for studying ferrimagnetism and ferrimagnetic properties.

Zinc ferrite belongs to the category of normal spinels [3]. The structural and magnetic properties

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of zinc ferrites have been the subject of study by various researchers over the last two decades. It has been established that structurally ZnFe_2O_4 is a normal spinel where it can be written as $(\text{Zn}^{2+})_A(\text{Fe}^{3+})_2\text{B}\text{O}_4$ and its net magnetisation is zero. Investigations on zinc ferrite indicated that zinc ferrite is antiferromagnetic because of B–B interactions with a Néel temperature of about 10 K [4]. Above the Néel temperature, it behaves as a paramagnet [4]. There have been reports indicating anomalies in the magnetic properties of zinc ferrite [5,6]. For instance, Lotgering et al. [5] detected anomalous behaviour in the paramagnetic susceptibility of zinc ferrite. Brock-house and others [6] found the presence of a short-range order of parallel spins separated by 0.29 nm in their neutron diffraction studies at 89 K. We undertook investigations on the structural and magnetic properties of zinc ferrite samples prepared by various techniques. Furthermore, the surface composition of the samples prepared by these two different techniques was investigated by low energy ion scattering (LEIS). Mössbauer spectroscopy was employed as an analytical tool to discern more information on the nature of ordering on these samples.

2. Experimental

2.1. Preparation of zinc ferrite at low temperature

Zinc ferrite was prepared by low temperature preparative techniques as described by Sato et al. [7]. 0.1 M aqueous solution of zinc nitrate and 0.2 M aqueous solution of ferric nitrate were prepared separately. 100 ml of each solution was mixed together, while stirring this mixture, 25% ammonia was added until the pH was between 9 and 11 at 320 K. The precipitate was dried at 373 K and calcined in air at 773 K which yielded zinc ferrite.

2.2. Preparation of zinc ferrite at high temperature

Zinc ferrite was also prepared by conventional ceramic technique [8]. Appropriate amounts of ZnO were mixed with freshly prepared alpha iron

oxide which in turn was prepared by using oxalate precursors. They were pre-fired at 773 K. The final sintering was carried out at around 1223 K for several hours.

2.3. LEIS experiments

The technique of low energy ion scattering (LEIS) is increasingly being used for the identification of surface stains and corrosion products, compositional depth profiling, surface study of oxides etc. Though it is complimentary to techniques such as AES and XPS, it has definite advantages over similar techniques. The advantage of employing LEIS are manifold. It enables the probing of clean surfaces. The data thus gathered yield information on atomic and electronic structures, surface composition of alloys and oxides.

The surface composition of zinc ferrite samples prepared by these two techniques was determined by LEIS. The characteristic feature of LEIS is that it is a powerful tool to probe the outermost layer of atoms on a material. This is an essential aspect that is useful in analysing oxidic spinels. The experiments were performed with LEIS instrument NODUS of which the basic design is illustrated elsewhere [9]. In this apparatus it is possible to compensate for surface charging by impinging thermal electrons over the surface from all sides. The base pressure in the UHV system was about 10^{-9} mbar and during operation it increases to 10^{-8} mbar. The polycrystalline powders used for the LEIS experiments were pressed into pellets in lead holders. A 3 keV $^4\text{He}^+$ ion beam was used for the measurements. The scattering conditions were kept constant during the measurements in order to facilitate comparison of data on an absolute level on different powder samples having different surface areas.

2.4. Magnetic measurements

Room temperature magnetic measurements were carried out using a VSM (model 4500) and parameters like saturation magnetisation (M_s), coercive force (H_c) and remanance (M_r/M_s) were evaluated.

2.5. Mössbauer studies

The ^{57}Fe Mössbauer spectrum of ZnFe_2O_4 was recorded at room temperature and also at 16 K using a constant acceleration Mössbauer spectrometer. A closed cycle He-refrigerator (CTI cryogenics model 226) was used to cool the absorber at 16 K.

2.6. X-ray diffraction studies

The crystal structure of ZnFe_2O_4 prepared by two different routes was determined by using X-ray powder diffraction techniques (XRD) (PW1140).

2.7. BET surface area

BET surface area of the samples were obtained on a micrometric ASAP 2400 adsorption system and subsequently the surface area of the samples were evaluated. The details of measurements are described elsewhere [10].

3. Results and discussion

The surface area of zinc ferrite samples prepared by two different routes are shown in Table 3. It shows that the sample prepared by a ceramic technique has a surface area of $0.92 \text{ m}^2/\text{g}$ while the sample prepared by a co-precipitation technique has a very large surface area of $29.6 \text{ m}^2/\text{g}$. The XRD analysis of these two samples are shown in Tables 1 and 2. The XRD patterns are indicative of the fact that the compounds are monophasic with no detectable impurities. The lattice parameter for these two compounds have been evaluated and were found to be 8.43941 and 8.4262, respectively, for ceramic and co-precipitation techniques. Magnetization measurements carried out on these samples showed a magnetization of 3.12 emu/g and coercivity of 62.5 Oe . This is an anomalous result in the sense that ZnFe_2O_4 crystallises in the normal spinel structure [3] where Zn^{2+} is found exclusively on the tetrahedral sites (A). Since zinc ferrite exhibits a net magnetisation of 3.12 emu/g , it is to be assumed that some amount of Zn occupies the B site. From LEIS measurements

Table 1

X-ray diffraction data for zinc ferrite prepared by low temperature techniques. Radiation: $\text{Cu-K}\alpha$, $\lambda[\text{\AA}^0]$: 1.5418

$d [\text{\AA}^0]$	Intensity ($I/I_0 \times 100$)	$h k l$
4.8478	17.1	1 1 1
2.9785	74.3	2 2 0
2.5391	100.0	3 1 1
2.4327	14.3	2 2 2
2.1081	40.00	4 0 0
1.7187	17.1	4 2 2
1.6234	57.10	5 1 1
1.4881	80.00	4 4 0
1.3357	8.6	6 2 0
1.2869	11.4	5 3 3

Table 2

X-ray diffraction data of the zinc ferrite prepared by ceramic technique. Radiation: $\text{Cu-K}\alpha$, $\lambda[\text{\AA}^0]$: 1.5418

$d [\text{\AA}^0]$	Intensity ($I/I_0 \times 100$)	$h k l$
4.8663	6.4	1 1 1
2.9824	36.4	2 2 0
2.5453	100.0	3 1 1
2.4359	7.1	2 2 2
2.1104	17.10	4 0 0
1.7232	12.1	4 2 2
1.6248	34.7	5 1 1
1.4929	42.1	4 4 0

(c.f. Table 3) it can be seen that some amount of Zn is detected on the surface. The amount of Zn detected on the ceramic sample is less than that of the zinc ferrite sample prepared by the co-precipitation method (c.f. Table 3). It must be mentioned in this context that low concentration of Zn on the surface cannot be attributed to a low sensitivity of LEIS for Zn because this is not the case for pure Zn where no matrix effects are expected [11].

Ziolkowski and Barbaux [12] have predicted through semi-empirical calculations that in the case of spinels like Co_3O_4 it is the A(1 1 1) and D(1 1 0) planes that are energetically preferred on the surface, whereas Shelef et al. [13] with the aid of LEIS

Table 3
Results of LEIS experiments and BET surface area

Sample	Method of preparation	Surface composition from LEIS experiments ($\# 10^3$)			BET surface area (m^2/g)
		O	Fe	Zn	
ZnFe ₂ O ₄	Ceramic	4.8	26.5	1.7	0.92
ZnFe ₂ O ₄	Co-precipitation	4.8	27.0	2.4	29.6

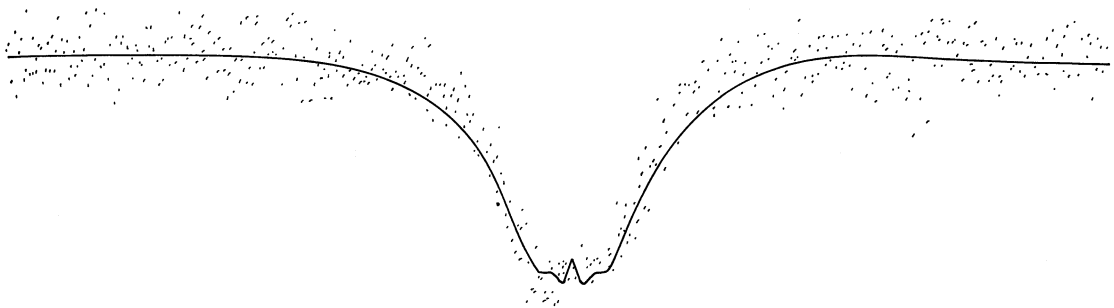


Fig. 1. Mössbauer spectrum of ultrafine zinc ferrite at 16 K.

concluded that tetrahedral sites are not on the surface. Jacobs et al. [14] and Anantharaman et al. [15] through independent experiments conducted on spinel aluminates and spinel ferrites, respectively, have established that it is the octahedral sites which are preferentially exposed on the surface of spinel compounds.

LEIS results indicate that the amount of zinc detected on the high surface area sample is much more than that detected on the sample prepared by the ceramic technique (Table 3). It has been proven by various researchers [12–15] that it is the octahedral sites that are preferentially exposed on the spinel surfaces. From LEIS it was found that the amount of Zn^{2+} in the B site increases with decrease in particle size. Thus the detection of Zn on the surface of zinc ferrite then leads to the conclusion that some amount of Zn occupies the octahedral sites, and the amount of zinc occupation is dependent on particle size. The finer the particles, the more the zinc on the B site. This observation using LEIS receives further evidence in the magnetic measurements conducted by Kamiyama et al.

[16]. Kamiyama et al. in their experiments have found that the finer the particles are, the more the saturation magnetisation is. They assumed a cation distribution of $\text{Zn}_{1-x}\text{Fe}_x[\text{Zn}_x\text{Fe}_{2-x}]\text{O}_4$, where $x = 0.04$ or more.

The Mössbauer spectrum at room temperature was satisfactorily fitted with a single doublet having a quadrupole splitting of 0.37 mm/s and centre shift of 0.33 mm/s. Since the fitted linewidth was only 0.30 mm/s, the presence of another doublet is ruled out. The Fe^{57} Mössbauer spectrum of ZnFe_2O_4 recorded at 16 K is shown in Fig. 1. The spectrum shows clearly that ZnFe_2O_4 is magnetically ordered at 16 K. The data was analysed by means of a procedure developed by Window [17]. In this method it is assumed that the observed line shapes arise from the probability distribution $P(H)$ of hyperfine fields. In Fig. 1 the dots represent the experimental data and the solid line is a result of the fitting of the data using the Window approach. The resultant probability distributions are shown in Fig. 2. The most probable field is found to be 63 kOe and the mean field of the

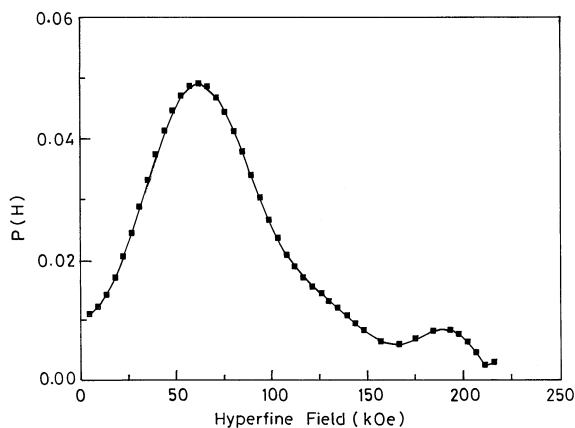


Fig. 2. Hyperfine field distribution in ultrafine zinc ferrite at 16 K.

distribution is 80 kOe. The magnetic ordering in ZnFe_2O_4 is possible only if there is an inversion, that is, some of the Zn^{2+} ions occupy the octahedral sites and some of the Fe^{3+} ions occupy the tetrahedral sites which give rise to a strong coupling between Fe^{3+} ions at A and B sites due to the A–B interaction.

This experimental observation receives further support from the studies conducted on ultrafine zinc ferrite particle by Sato et al. [6]. In their experiments, they found that the saturation magnetisation of ultra fine zinc ferrite particles increases with a decrease in particle size at room temperature. They observed the same trend at low temperature. Furthermore, EXAFS studies conducted on zinc ferrites by Jayadevan et al. [19] also support the presence of Zn^{2+} on the B site. Thus it is reasonable to conclude that the Fe^{3+} situated on A sites, according to cation distribution $\text{Zn}_{1-x}\text{Fe}_x[\text{Zn}_x\text{Fe}_{2-x}]\text{O}_4$ forms a cluster with its 12 nearest Fe^{3+} neighbours at B sites through coupling. Probably the number of clusters increases with decreasing particle size. So anomalous magnetisation may be due to the short-range ordering of the samples as reported by Schiessel et al. [18] and Kamiyama et al. [15]. However, it must be mentioned that the surface spins may also contribute to the observed magnetisation as they are expected to be considerably high in number due to small size of particles.

4. Conclusions

LEIS experiments conducted on ZnFe_2O_4 samples prepared by two different techniques having different particle sizes revealed that an amount of Zn occupies the octahedral sites. The amount of zinc detected on the surface of high surface area zinc ferrite is higher than that of the low surface area zinc ferrite prepared by the ceramic technique. This establishes that zinc substitution increases with decreasing particle size. Mössbauer results show that the A–B interactions are not long ranged but only short ranged.

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