Magnetic ordering in $\text{Mg}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ system

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Abstract. Magnetization measurements of the ferrite system $\text{Mg}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ were undertaken primarily to study variation of the saturation magnetization with manganese concentration and to gain information about the type of magnetic ordering. The observations indicate the existence of Yafet-Kittel (YK) type of magnetic ordering in this system which is well supported by results of Mössbauer effect measurements. A molecular field analysis of the YK spin ordering using the three-sublattice model is shown to explain the experimental data satisfactorily.

Keywords. Ferrites; magnetic ordering; collinear; non-collinear.

1. Introduction

This possibility of changing continuously the concentration of non-magnetic ions in the different sublattices makes the ferrites very interesting materials to study the appearance of various magnetic structures (Bhargava and Zeeman 1980; Brand et al 1985; Muralidharan et al 1985; Dormann et al 1987; Chakravarthy et al 1988; Dormann and Nogues 1990; Jotania et al 1992). Among these, systems with spinel structure seems to be particularly attractive, as they allow a variety of magnetic disorder and frustration to be introduced. This is due to the fact that, in spinel intra-sublattice interactions are weaker than the inter-sublattice interactions, as a result there are unsatisfied bonds in the ferrimagnetic phase. Because of these unsatisfied bonds increasing magnetic dilution accentuates the competition between the various exchange interactions resulting in a variety of magnetic structures (Bhargava and Zeeman 1980; Brand et al 1985; Muralidharan et al 1985; Dormann et al 1987; Chakravarthy et al 1988; Dormann and Nogues 1990; Jotania et al 1992).

A large number of investigators have studied Ti-substituted spinels in order to understand their magnetic properties. Brand et al (1985) found in the case of $\text{Mg}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ that on increasing dilution $x$, the collinear ferrimagnetic phase breaks down before reaching the ferrimagnetic percolation threshold and for higher concentration of Ti, system approaches toward spin-glass. Dormann et al (1987) have also studied the magnetization measurements of Ti$^{4+}$ substituted lithium ferrite using different techniques and suggested the possibility of canted spin arrangements to explain the magnetization measurements.

In order to understand the influence of magnetic ion Mn$^{4+}$ in place of non-magnetic ion Ti$^{4+}$, we have modified the magnetic phase of $\text{Mg}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ by replacing Ti$^{4+}$ by Mn$^{4+}$, so that intra-sublattice interaction ($J_{\text{hh}}$) will become predominant over the inter-sublattice interaction ($J_{\text{ab}}$), which may lead to a frustration in the spin sub systems. In our recent communication (Jani et al 1997), we have reported magnetic properties on the mixed spinel $\text{Mg}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$. The present paper reports the results of X-ray, magnetization and Mössbauer effect measurements on the $\text{Mg}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ system. The variation of the saturation magnetization per formula unit in Bohr magneton number ($n_B$) with Mn-concentration in this system is similar in nature to that in the Ni–Zn (Satyamurthy et al 1969) and Cu–Zn (Kulkarni and Patil 1982) ferrites and the existence of Y–K angles on the B-site, observed in the latter systems is strongly suspected. A molecular field analysis of the Y–K spin ordering using a three-sublattice model is shown to explain the experimental data satisfactorily.

2. Experimental

Nine samples of Mn-substituted $\text{Mg}_{1+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ system were prepared by the usual double sintering ceramic method for $0.1 \leq x \leq 0.9$ in steps of 0.1. The starting materials were analytical reagent grade oxides, Fe$_2$O$_3$, MgO and MnO. These oxides were mixed in proper proportions and presintered at 990°C for 24 h. In the final sintering process the material was held at 1050°C for 12 h and slowly cooled to room temperature (2°C/min). The X-ray diffractograms were obtained using FeK$_\alpha$ radiation on a Philips X-ray diffractometer model PW-1820. The diffraction patterns show the sharp lines corresponding to a single phase spinel for all the samples.
The magnetization measurements of each sample at 300 K were carried out using high-field hysteresis loop technique (Radhakrishnamurthy et al 1971). The Mössbauer spectra were obtained at 12 K and 300 K in transmission geometry with source of 10 mCi $^{57}$Co(Pd) and a constant acceleration transducer interface to PC-based 1024 multi channel analyser.

3. Results and discussion

All the compositions of the system $\text{Mg}_{1+x} \text{Mn}_x \text{Fe}_{2-z} \text{O}_4$ exhibit single phase cubic spinel structure. No reflections other than those belonging to a spinel structure were observed in the patterns (figure 1). The values of lattice constant ‘a’ (Å) determined from X-ray data with an accuracy of ±0.002 Å for $x=0.1$ to 0.9 are shown in figure 2 as a function of $x$. It is clear from figure 2 that the ‘a’ parameter initially increases up to $x=0.4$ and thereafter it levels off for further increase in $x \geq 0.5$. The observed nonlinear behaviour in ‘a’ with $x$ may be attributed to the simultaneous replacement of $\text{Fe}^{3+}$ (0.64 Å), $\text{Mg}^{2+}$ (0.60 Å) and $\text{Mn}^{4+}$ (0.60 Å). The cation distribution of $\text{MgFe}_2\text{O}_4$ ($x=0$) has been reported to be

$$(\text{Mg}_{0.08}\text{Fe}_{0.92})^A [\text{Mg}_{0.92}\text{Fe}_{1.08}]^B \text{O}_4, \quad (1)$$

where A is the tetrahedral site and B the octahedral site. In order to determine the cation distribution, XRD intensities were calculated using the formula suggested by Buerger (1960):

$$I_{hkl} = I_{F_{hkl}} P L_p, ~ (2)$$

where notations have their usual meanings. The distribution of divalent, trivalent and tetravalent cations amongst octahedral and tetrahedral sites in the $\text{Mg}_{1+x} \text{Mn}_x \text{Fe}_{2-z} \text{O}_4$ samples are determined from the ratios of intensities of X-ray diffraction lines: $I_{220}/I_{440}$, $I_{220}/I_{400}$ and $I_{400}/I_{422}$. In table 1, the results of X-ray intensity calculations for typical samples $x=0.2$, 0.6, 0.8 and 0.9, are listed along with experimental intensity ratios. It is evident from table 1 that tetravalent Mn-ions occupy B-site replacing B-site iron and the added $\text{Mg}^{2+}$ ions substitute for A-site iron without any change with $x$ in the initial degree of inversion i.e. (1).

In deriving the cation distribution of $\text{Mg}_{1+x} \text{Mn}_x \text{Fe}_{2-z} \text{O}_4$ our X-ray intensity calculations (table 1) and relative $\text{Fe}^{3+}$ intensities of Mössbauer spectra (table 2), for A and B site ions were taken into account. Accepting the cation distribution of $\text{MgFe}_2\text{O}_4$ (1), an approximate cation distribution for the $\text{Mg}_{1+x} \text{Mn}_x \text{Fe}_{2-z} \text{O}_4$ can be written as

![Figure 1. Typical X-ray diffractograms of the system $\text{Mg}_{1+x} \text{Mn}_x \text{Fe}_{2-z} \text{O}_4$ for $x=0.2$, 0.6, 0.8 and 0.9.](image)

![Figure 2. Variation of lattice parameter a (Å) with Mn concentration x.](image)