High field magnetization studies in lithium-zinc ferrite[a]

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The magnetization in $Li_{0.5-z/2}Zn_zFe_{2.5-z/2}O_4$ with $z = 0.0$, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 has been measured at 30 K and at applied magnetic fields of up to 100 kOe. The magnetization for samples with $z \leq 0.2$ saturated at less than 10 kOe. The magnetization for samples with $z \geq 0.3$ did not saturate. Rather, for applied fields in excess of 30 kOe, these samples exhibited field-independent differential susceptibilities ranging from 1.68×10^{-5} emu/g-Oe for $z = 0.3$ to 20.66×10^{-5} emu/g-Oe for $z = 0.7$. The high-field susceptibilities are attributed to localized canting of octahedral site Fe^{3+} spins with fewer than three tetrahedral site Fe^{3+} nearest neighbors. Susceptibilities predicted by existing localized canting models are in qualitative agreement with the data, but predicted values for large z are too small.

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INTRODUCTION

Based on the cation distribution [1]

$$Zn_z^{2+}Fe_{1-z}^{3+}[Li_{0.5-z/2}^{1+}Fe_{1.5+z/2}^{3+}]\,O_4^{2-},$$

Zn addition is expected to increase the net moment in Li ferrite through enhancement of the Fe^{3+} content of the dominant octahedral B sites relative to that of the tetrahedral A sites. In actuality, the addition of more than about 0.4 atoms of Zn per formula unit of Li ferrite results in a decrease in the magnetization σ [2]. Similar behavior has been observed in other spinel ferrites and in substituted garnets.

Several models have been proposed to explain this discrepancy. All are based on a departure from parallel alignment for the B spins, due to a Zn induced reduction in the normally dominant antiferromagnetic A-B exchange interaction. These models may be classified into two categories: (1) that in which some or all of the B spins cant relative to each other [3,4], and (2) that in which the B spins do not cant, but in which some of the B spins are aligned parallel to the A spins and some of the B spins may be paramagnetic [5,6,7]. The existence of spin canting has been confirmed by Mössbauer studies in Co-Zn ferrites [8], and through neutron diffraction and Mössbauer studies in Ni-Zn ferrites [9,10]. High-field magnetization data in several chromite spinels are also consistent with the presence of spin canting in these systems [11].

Interpretations of various data in Li-Zn ferrites do not agree on the existence of canting. The neutron diffraction data of Zhilyakov et al. [12] are consistent with spin canting. However, Young and Smit [13] obtained a reasonable fit to zero-field room temperature Mössbauer and magnetization data merely by assuming B site spins, with less than two A site Fe^{3+} nearest neighbors, to be flopped. Mössbauer data in applied fields of up to 15 kOe are inconclusive with respect to canting [14].

In this investigation the magnetization σ in polycrystalline $Li_{0.5-z/2}Zn_zFe_{2.5-z/2}O_4$ with $0 \leq z \leq 0.7$ has been measured at 30 K and at applied fields H_o of up to 100 kOe. The data support the spin canting hypothesis and have been analyzed in terms of two specific canting models: the uniform canting model of Yafet and Kittel [3] (hereafter referred to as the Y-K model), and the localized canting model of Rosencwaig [15]. The Y-K model appears to be inconsistent with the high field data. Some sort of localized canting appears to be operative, but none of the existing localized canting models are in quantitative agreement with the data.

EXPERIMENT

Measurements of σ vs. H_o were made with two vibrating sample magnetometers. High-field data were obtained for $0 \leq H_o \leq 100$ kOe by vibrating the sample along the axis of a superconducting solenoid. Data were also obtained over the low-field range of $0 \leq H_o \leq 8$ kOe, with a commercial VSM. The sample temperature for the high-field measurements was maintained at 30 K by flowing cold He gas over the sample. For the low-field measurements, the sample temperature was maintained at 4 K in a commercial temperature-stabilized dewar system.

The samples consisted of hot-pressed polycrystalline Li-Zn ferrite materials [16], $Li_{0.5-z/2}Zn_zFe_{2.5-z/2}O_4$, with z = 0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7. The preparation of these materials has been described elsewhere [17].

EXPERIMENTAL RESULTS

Data of σ at 30 K vs. H_o up to 100 kOe are shown in Fig. 1. For $z \leq 0.2$, σ is independent of H_o. For $z \geq 0.3$ however, the magnetization does not saturate, but increases with H_o up to the maximum applied field. The incremental susceptibility χ_{hf} is field independent above 30 kOe for all samples. For $z \geq 0.5$, there also appears to be a second linear region at low field, 10 kOe $\lesssim H \lesssim$ 30 kOe, with a differential susceptibility χ_1 which is greater than χ_{hf}. The zero-field extrapolated magnetizations are shown in Fig. 2. For $z < 0.4$, σ increases with z. For $z \geq 0.4$, σ decreases with increasing Zn concentration as previously reported [2,12].

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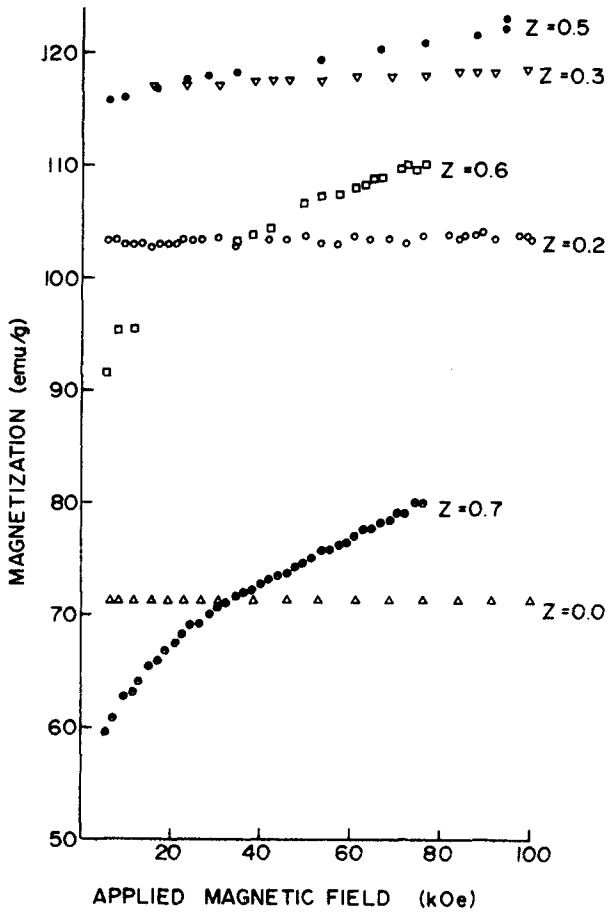

Fig. 1. Magnetization in $Li_{0.5-z/2}\ Zn_z\ Fe_{2.5-z/2}\ O_4$ at 30 K vs. applied magnetic field H_o for samples with various amounts of Zn.

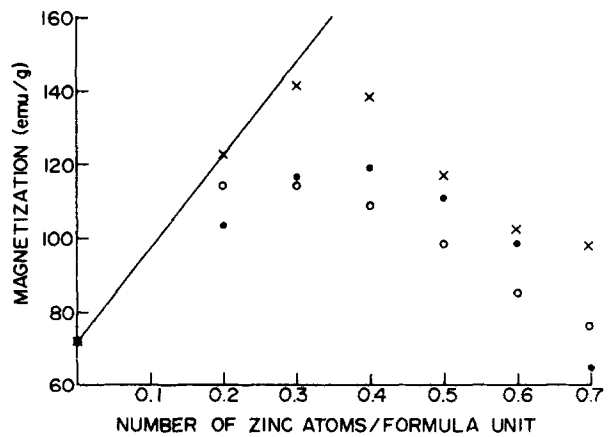

Fig. 2. Zero-field extrapolated magnetization as a function of Zn concentration z in $Li_{0.5-z/2}\ Zn_z\ Fe_{2.5-z/2}\ O_4$:
· indicate experimental data,
× indicate theory with $\delta = 0.28$,
o indicate theory with $\delta = 0.33$,
- indicate theory based only on Fe^{3+} distribution.

As shown in Table I, both the high-field incremental susceptibility χ_{hf} and the intermediate field incremental susceptibility χ_i increase with increasing z. Values of χ_{hf} range from 2×10^{-5} emu/g-Oe at $z = 0.3$ to 21×10^{-5} emu/g-Oe at $z = 0.7$. The χ_i range from 9×10^{-5} emu/g-Oe at $z = 0.5$ to 47×10^{-5} emu/g-Oe at $z = 0.7$.

Data recently reported by Zhilyakov et al. [12] at 4.2 K and applied fields up to 20 kOe are also shown in Table I. The present values of χ_{hf} are much smaller than the Zhilyakov values. For high Zn concentrations, the Zhilyakov values appear to correlate reasonably well with the present values of χ_i. The differences in susceptibilities at lower Zn concentrations, and especially at $z = 0.2$, are not reconcilable. To ascertain that the null value of χ_{hf} for $z = 0.2$ at 30 K was not due to a temperature effect, σ vs. H_o was measured for this sample at 4 K in fields up to 8 kOe. The resolution of this measurement was limited by the restricted range of applied field. Nevertheless, the susceptibility measured this way was less than 10^{-4} emu/g-Oe, which is significantly smaller than the Zhilyakov value.

DISCUSSION

Of the possible spin structures, the field-independent high-field susceptibilities for $z \geq 0.3$ are most consistent with a spin canting model. The large variation in χ_{hf} with Zn content however, is inconsistent with the Y-K model, which predicts a nearly composition-independent χ_{hf}. Furthermore, the change in incremental susceptibility with field for samples with $z \geq 0.5$ is not predicted by this model. Given that the Zn distribution is probably random over the A sites, such problems with a uniform canting model are not surprising.

Both the z dependence of χ_{hf}, and the transition in slope from χ_i to χ_{hf} in samples with $z \geq 0.5$ are qualitatively more consistent with some sort of localized canting model. Based on local field considerations and the exchange parameters reported by Srivastava et al. [18] for Li-Zn ferrites, it is likely that canting is primarily localized to those B sites with fewer than three A site Fe^{3+} nearest neighbors. This assumption is supported by the fact that χ_{hf} normalized to the probability that a particular B site Fe^{3+} has two or less A site nearest neighbors [13] is nearly independent of z (cf. Table I). This suggests that such sites make roughly equivalent contributions to χ_{hf}.

Within the local canting scheme, the transition from χ_i to χ_{hf} can qualitatively be attributed to a saturation effect in which some of the weakly canted configurations are straightened out at moderate fields. Alternatively, similar behavior in substituted garnets has been attributed [19] to a high anisotropy of regions which have become locally antiferromagnetic.

Quantitative localized canting models have been developed by Nowik [20] and Rosencwaig [15] to explain zero-field magnetization data, qualitatively similar to that in Fig. 2, in substituted garnets. In these models, the spin on a particular B site sees an effective exchange field consisting of the A site intersublattice field, and a B site field which is canted at the average canting angle. The Rosencwaig model has been adapted to the case at hand, with the external applied field added to the A site intersublattice exchange field. In this model, the relevant parameter is $\delta \equiv J_{bb}/J_{ab}$, the ratio of the intrasublattice to intersublattice exchange constants. Predicted values for the magnetization in zero field are plotted along with the experimental data as a function of Zn content z in Fig. 2. The theoretical values of σ were calculated using $\delta = 0.28$, which corresponds to the exchange constants reported for Li ferrite by Srivastava et al. [18], and $\sigma = 0.33$ which gave the best overall agreement, of several tried, with the data.

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TABLE I

Measured high-field dc susceptibilities in $Li_{0.5-z/2}Zn_zFe_{2.5-z/2}O_4$. The values under χ_Z are those reported by Zhilyakov et al. [12]. The values under χ_N are the values of χ_{hf} divided by the probability that a B site spin has less than three A site Fe^{3+} nearest neighbors.

z	χ_{hf} $\times 10^{-5}$ emu/g-Oe	χ_i $\times 10^{-5}$ emu/g-Oe	χ_Z $\times 10^{-5}$ emu/g-Oe	χ_N $\times 10^{-5}$ emu/g-Oe
0.0	0	0	0	0
0.2	0	0	29	0
0.3	2	0	34	24
0.4	3	0	36	16
0.5	7	9	40	20
0.6	15	27[a]	46	26
0.7	21	47	59	28

[a]Measured at 16 K.

Agreement between the differential susceptibilities predicted by the extended Rosencwaig model and those observed is only fair. The theory does predict field-independent high-field differential susceptibilities which increase with increasing Zn content. Also, the predicted χ_{hf}, for $z = 0.3$ and $\delta = 0.33$, of 1.5×10^{-5} emu/g-Oe is in good agreement with the observed value of 2×10^{-5} emu/g-Oe. However, for both $\delta = 0.33$ and $\delta = 0.28$, the theoretical z dependence is far too weak, with the predicted value of χ_{hf} at $z = 0.7$ only one-tenth the observed value. Furthermore, this theory does not predict the transition from χ_i to χ_{hf} observed in materials with $z \geq 0.5$.

SUMMARY

The high-field susceptibilities reported here, and the neutron diffraction data of Zhilyakov et al. [12], provide strong evidence in favor of canting of the B site spins due to Zn substitution in Li ferrite. These data further suggest that the canting occurs for B site spins with fewer than three A site Fe^{3+} nearest neighbors. The Rosencwaig model of localized canting provides reasonable agreement with the zero-field magnetization data. As extended here, it also predicts correct susceptibilities for low level Zn substitutions. At higher levels however, the model is less successful. The predicted susceptibilities are much too low, and the transition from χ_i to χ_{hf} is not predicted.

Although the qualitative nature of the spin canting in Li-Zn ferrites is reasonably clear, existing quantitative models are inadequate. The source of failure in these models is not presently obvious, but it may lie in the manner in which the B molecular field is treated. It is doubtful that any B spin actually sees a B-B molecular field which is characterized by the average canting angle. Rather, it is more likely that each B spin sees a specific combination of other B spins. In this context, it is reasonable that the susceptibilities of B spins with distinct B environments will also be distinct. Consequently, an approach which averages over the more prominent of such individual terms might prove fruitful.

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