ORDER-DISORDER EFFECTS IN THE ANISOTROPY OF SUBSTITUTED LITHIUM FERRITE

C. J. Brower and C. E. Patton

ABSTRACT

In pure lithium ferrite, octahedral (B) site cation ordering is known to affect the first-order anisotropy constant K_1. Investigations of Co- and Mn-Co-substituted Li ferrite have now revealed changes in K_1 concurrent with ordering which are much larger than those occurring in pure Li ferrite. The spinwave linewidth ΔH_k also exhibits large changes. These effects have not been reported to date. The large changes with disorder are found to arise from migration of Co to the tetrahedral (A) sites. Low level Mn substitutions are found to modify Co behavior. Manganese-induced oxidation of Co^{2+} to Co^{3+} is shown to be a plausible mechanism.

INTRODUCTION

Lithium ferrite is a ferrimagnetic inverse spinel with the octahedrally coordinated interstitial sites (B sites) occupied by both Li^+ and Fe^{3+} ions. These cations can exhibit unique atomic ordering [1], which is known to affect the first-order anisotropy constant K_1 in pure Li ferrite [2]. Investigations of Co- and Mn-Co-substituted Li ferrite have now revealed changes in K_1 concurrent with ordering which are much larger than those occurring in pure Li ferrite. The spinwave linewidth ΔH_k also exhibits large differences. These effects have not been reported to date.

EXPERIMENT

Nine materials were investigated. Four were substituted simultaneously with Co (0.02 Co ions/formula unit) and Mn (0, 0.025, 0.050, and 0.100 Mn/F.U.). The balance were Mn substituted only (0, 0.0125, 0.025, 0.050, and 0.100 Mn/F.U.). All samples were polished and annealed spheres, with the annealing used for both stress relief and (dis)ordering. The samples were ordered with a four-hour anneal in air at 700°C, followed by a slow cooling (33°C/hour). After measurement, they were disordered by annealing at 900°C for one-half hour and quenched in H_2O at 20°C.

The anisotropy field H_a was measured as a function of temperature using a previously reported FMR technique [3]. The spinwave linewidth ΔH_k at 20°C was also measured. An 8.9 GHz magnetic pump field was applied parallel to a DC bias field. ΔH_k was derived from observation of the microwave field amplitude necessary for the onset of spinwave instability processes.

RESULTS

Figure 1 shows H_a as a function of temperature for simultaneous Co and Mn substitutions in both the ordered and disordered states. Manganese is commonly used in polycrystalline Li ferrite to oxidize Fe^{2+}. Usable H_a results were not obtained from the sample with no Mn due to the large conductivity induced (Fe^{2+}) linewidth. Figure 2 shows ΔH_k (in the $k \to 0$ limit) as a function of Mn level for both order and disorder. Results are given for samples both with and without Co.

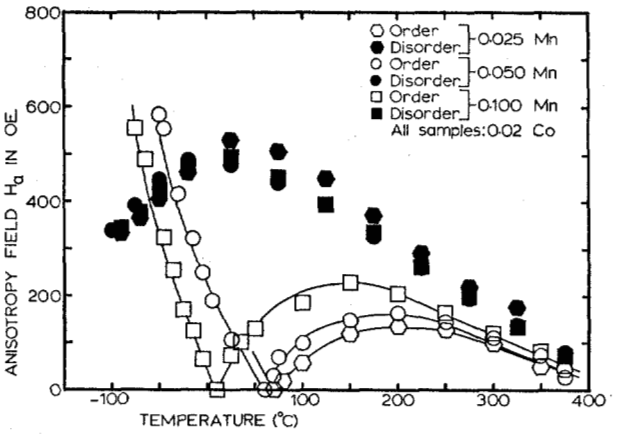

Fig. 1. Anisotropy field H_a vs. temperature for Mn-Co-substituted Li ferrite in both ordered and disordered states.

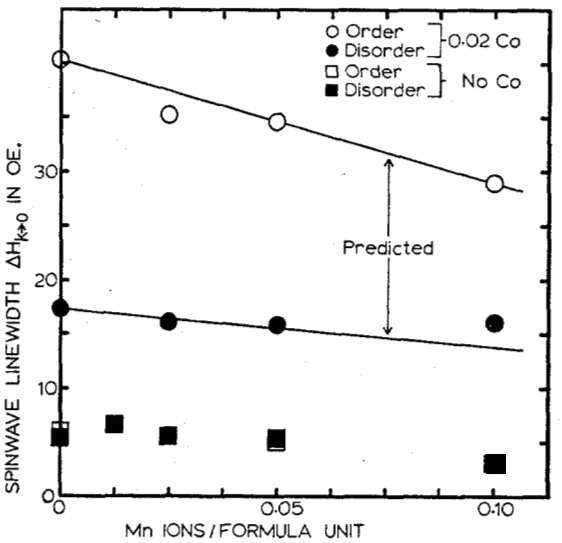

Fig. 2. Spinwave linewidth ΔH_k in the $k \to 0$ limit vs. Mn substitution level. Data are shown for samples both with and without Co in the ordered and disordered states. The predicted behavior comes from assuming B site Co^{2+} is oxidized to Co^{3+} when it has a Mn nearest neighbor.

As evident from Fig. 1, there is a substantial change in the anisotropy field concurrent with disorder for 0.02 Co/F.U. Figure 3 shows the temperature dependence of the first order anisotropy constant K_1 in pure Li ferrite, for both ordered and disordered states. Figure 4 shows this K_1 data for the Co-substituted material. The difference in K_1 between

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ordered and disordered states is considerably larger for the Co-substituted case. A plausible initial hypothesis might associate the effects observed for Co substitutions with the change exhibited by the pure material. The observed behavior could also be explained by migration of Co from B sites to A sites. The latter mechanism will be discussed first.

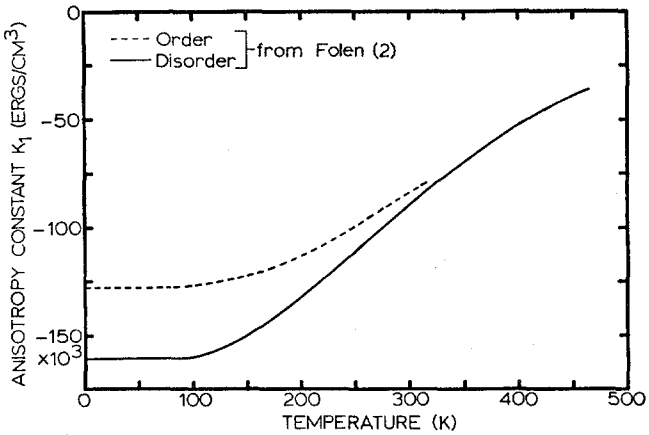

Fig. 3. First order anisotropy constant K_1 vs. temperature for pure Li ferrite in both ordered and disordered states.

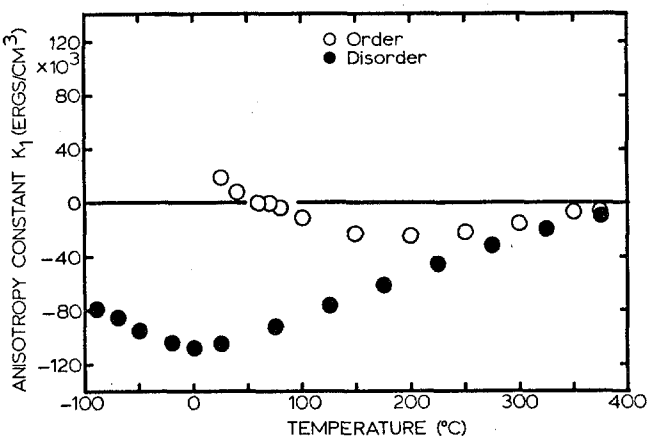

Fig. 4. K_1 vs. temperature for Co-substituted (0.02 Co/F.U.) Li ferrite in both ordered and disordered states.

In the spinel structure, the magnetic ions experience a crystalline electric field of primarily cubic symmetry. At the B sites, this field is trigonally distorted (due to A-site ion placement). Co^{2+} is normally expected to reside on B sites. The trigonally distorted field at these sites establishes a ground state doublet in Co^{2+}. This is what produces the exceptionally large anisotropy observed for Co^{2+} ions [4,5,6]. Any Co^{2+} residing on A sites would have a ground state singlet [7]. The anisotropy contribution of A-site Co^{2+} would thus be orders of magnitude less than that of B-site Co^{2+}.

Although Co^{2+} has a site preference energy favoring B sites at room temperature [8], it can be quite mobile at higher temperatures [9,10]. Any Co migrating to A sites at elevated temperatures would be frozen into place when the specimens were quenched to preserve disorder. The Co^{2+} locked into the A sites would make a negligible contribution to the anisotropy. In terms of the anisotropy, the Co^{2+} concentration would be effectively reduced by the amount which migrated to the A sites. A comparison with published single-crystal anisotropy data [4] indicates that the 0.02 Co/F.U. disordered Li ferrite is behaving as if its substitution level is only 0.006 Co/F.U. The migration hypothesis would assert that 2/3 of the Co has migrated to A sites.

The migration hypothesis can be corroborated using spinwave linewidth data. ΔH_k should be sensitive to Co migration. The ground state doublet of B site Co^{2+} causes it to act as a (microwave) slow relaxer [11,12]. This shows up dramatically as an increase in ΔH_k as shown in Fig. 2. If Co migrates to A sites, the relatively large separation between the ground state singlet and the next lowest energy level should prevent it from acting as a slow relaxer. Any A-site Co would thus make a negligible contribution to ΔH_k.

The contribution of Co to ΔH_k can be obtained by subtracting the value in pure Li ferrite from that of the Co substituted material (using 0.0 Mn/F.U., Fig. 2). After disordering, the Co contribution to ΔH_k is approximately one-third as large as for the ordered state. The disordered material behaves as if it has an effective Co concentration of 0.007 Co/F.U., which agrees well with the K_1 observations.

Another possible explanation for the observed anisotropy effects would involve a mechanism similar to that which causes the observed changes in pure Li ferrite. The difference in anisotropy between ordered and disordered states (for pure Li ferrite) can be accounted for by considering the behavior of the crystalline electric field. In the ordered state, every B-site Fe^{3+} experiences the same local crystal field. In the disordered state, Li^+ is distributed randomly among the B sites. As a result, the B site Fe^{3+} ions experience a local crystal field which varies from site to site. The anisotropy contribution of each B site Fe^{3+} will depend upon the configuration of its "nearest neighbors" (NN).

The increase in anisotropy with disorder can be quantitatively predicted by estimating the B-site Fe^{3+} anisotropy contributions for the various NN configurations, and taking an average which is weighted by frequency of occurrence [13]. Application of this "local field" model to the Co-substituted case, however, predicts that the site-to-site variation of the local crystal field for disorder should increase the Co^{2+} anisotropy contribution slightly [13]. The local crystal field variation which causes the anisotropy change with disorder in pure Li ferrite, then, can not account for the observed effects of the Co-substituted material.

Figures 1 and 2 demonstrate another effect: Mn substitutions modify the behavior of Co. From single-crystal data, low level Mn substitution is expected to have little effect on K_1 [14]. A steady decrease in the anisotropy compensation temperature with Mn addition is displayed in Fig. 1, however.

Mn is added to polycrystalline Li ferrite to oxidize Fe^{2+}. It resides on the B sites [8]. A feasible explanation of the observed effects is that Mn is also oxidizing Co^{2+}: $Co^{2+} + Mn^{3+} \rightarrow Co^{3+} + Mn^{2+}$. Co^{3+} has a ground state singlet in a trigonally distorted cubic field [7]. Its anisotropy contribution should be orders of magnitude less than that of Co^{2+} and behave similarly to Fe^{2+}, also a $3d^6$ ion. The separation between the ground state singlet and the next lowest energy level should also be large enough to prevent Co^{2+} from acting as a slow relaxer.

A quantitative check on these predictions can be made. The probability of a B-site Co having at least one Mn NN can be calculated by assuming a random B-site distribution of Mn ions. Assuming that Co^{2+} is always oxidized in the presence of a Mn NN, the effective Co^{2+} concentration is then known as a function of Mn level. Figure 2 (ordered) shows the predicted results of this effective concentration

reduction on ΔH_k; agreement with the data is good. At 0.1 Mn/F.U., ΔH_k indicates an effective concentration of 0.015 Co^{2+}/F.U. From the K_1 data at 60°C (ordered, 0.1 Mn/F.U.), the effective concentration appears to be 0.014 Co^{2+}/F.U., which also agrees well with the predicted results.

A reduction in Mn-induced effects is expected with disorder if only one-third of the Co remains on B sites, as discussed above. This shows up in the ΔH_k data for disorder in Fig. 2. The size of the Mn-induced effect can be predicted in the same manner as for the ordered state. The predicted effect of Mn acting on this reduced concentration is shown in Fig. 2. Agreement with the data is good. The expected reduction in Mn-induced effects also shows up in the H_a data (Fig. 1). H_a data for disorder demonstrates little dependence on Mn level.

DISCUSSION

The observed changes in anisotropy with disorder stem from different mechanisms in pure Li ferrite and Co-substituted Li ferrite. In pure Li ferrite, the changes arise from site-to-site variations in the crystal field. In Co-substituted material, the Co is apparently migrating to A sites at the higher temperatures used to induce disorder. This migration explains the effects observed in both K_1 and ΔH_k. An interesting parallel occurs in Co ferrite. Mössbauer spectra indicate that its Co site distribution is dependent on thermal history [15,16]. Slowly cooled $CoFe_2O_4$ powder had 7% of the Co on A sites, with the balance on B sites. In powder quenched from 1200°C, however, 24% of the Co was left on A sites.

This thermal history dependence of the Co site distribution in Li ferrite is much stronger than might be expected. The dependence was discovered after routine stress relief annealing. Specimens had been annealed at 800°C for one-half hour, then cooled to ambient over a three-hour period. This was found to leave approximately one-half of the Co on A sites. Apparently, both Co site distribution and B site cation ordering are dependent on thermal history. The two effects are not necessarily related, however.

The Co-induced affects are diminished when Mn is present. Mn^{3+} is a Jahn-Teller ion. Mn clustering is thus expected to compete with B-site ordering. A substitution level of 0.25 Mn/F.U. is sufficient to remove all B site order [17]. Although Mn cluster-induced disorder could modify Co-induced behavior, it can not be the dominant effect. As discussed previously, the local field variation stemming from disorder increases the Co^{2+} anisotropy contribution slightly. Mn additions, however, are found to reduce the effectiveness of Co^{2+}. Oxidation of Co^{2+} by Mn^{3+} NN seems to be the most plausible explanation of the observed behavior in Mn-Co-substituted Li ferrite. Quantitative predictions made by assuming oxidation agree well with the data. This quantitative agreement also suggests that Mn clustering is minimal at these substitution levels. Clustering of the Mn should reduce the possibility of Co having a Mn NN. If a significant portion of the Mn ions were clustering, then the predictions made by assuming a random distribution of Mn ions should not have agreed with the data.

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