INTRA SITE CATION ORDERING AND CLUSTERING IN NATURAL Mn-Zn FERRITES

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ABSTRACT

Cooling rates of 10^{-3} K/yr. permit naturally occurring Mn-Zn ferrites (franklinites) to be in thermodynamic equilibrium at ambient temperatures with respect to both electrostatic and elastic energies. The elastic strain energy resulting from the occupancy of the A sites by ions of differing sizes is minimized by clustering of Mn and Zn in different regions of a crystal. Using ^{57}Fe NGR, these regions have been observed directly in franklinite with low Mn^{3+} contents and their structures elucidated. The Mn rich region has a local crystal chemistry very similar to that of $MnFe_2O_4$ and the Zn rich region has a local structure similar to that of $ZnFe_2O_4$. The two regions are crystallographically coherent. Laboratory heat treatments destroy the Mn-Zn ordering and alter the magnetic properties. The Fe spin configurations are also observed to be collinear. The discovery of the intrasite ordering in these materials proves that Goodenough's criteria for square B-H loops in ferrites can be realized. For samples containing Mn^{3+}, the effects of the Jahn-Teller distortions do not permit a direct observation of Mn-Zn intrasite ordering.

INTRODUCTION

Direct evidence for the proposal that the square B-H loops in ferrites can result from chemical inhomogeneities in grains without crystallographic discontinuities[1] has been lacking. Recent reviews[2] of materials for ferrite memory cores indicate that this proposal is still without a firm experimental basis despite the considerable volume of indirect evidence[3,4]. In addition to grain boundaries, Goodenough has shown that chemical inhomogeneities can also serve as nucleation sites for reverse domains.[1] The chemical inhomogeneity believed to be responsible for the square loops in actual memory core ferrites is clusters of Jahn-Teller ions such as Cu^{2+} and Mn^{3+}. Above some critical concentration, the local Jahn-Teller distortions of Mn^{3+} and Cu^{2+} will interact cooperatively to distort the spinel structure from cubic to tetragonal symmetry. Below this critical concentration, the distortions are uncorrelated and the elastic strain energy is rather large. The clustering of the Mn^{3+} and Cu^{2+} ions results in a decrease in the elastic strain; the Jahn-Teller distortions play no critical role in the magnetization processes. The requirement that the cluster regions have the same cubic symmetry as the surrounding spinel matrix seems, however, to contradict the very basis on which the clustering is predicated.

Chemical inhomogeneities resulting from clusters of S-state ions would provide a better fit to the theoretical model. Clustering of S-state ions is driven primarily by differences in size, charge state or both, but the enthalpy change associated with such clustering or ordering is rather small for 2-3 spinels such as the Mn-Zn ferrites and is likely to be smaller in magnitude than the $T\Delta S$ entropy term at temperatures where ion diffusion is sufficient to permit clustering to occur. Clustering has been observed to occur in

Sb^{5+} substituted $LiFe_5O_8$[5] but in this material the oxidation numbers of the ions differ by 4.

For sufficiently slow cooling rates over a broad temperature range, clustering is expected to occur even in 2-3 spinels. The lowest cooling rates are observed in natural metamorphic settings and evidence for the existence of clustering in natural Mn-Zn ferrites are presented in this paper. Mn-Zn ferrites occur in nature as the mineral franklinite. The occurrence of franklinites as fissure-and inclusion free octahedra with edges as much as 5 cm in length and having very narrow composition ranges is evidence of their having being slowly cooled over several thousands years, at least. Further evidence for the thermal equilibrium of franklinites is provided by the macroscopic geologic parameters of the deposit in which they occur.[6]

EXPERIMENTAL

^{57}Fe nuclear gamma-ray resonance(NGR) measurements, x-ray powder and single crystal diffraction measurements and wet chemical analysis were performed on five specimens of franklinites. Specimens were chosen primarily on the basis of crystal perfection, with composition being of secondary importance. A typical octahedral crystal weighed approximately 150 gm and was about 3 cm long on each edge. Thin sections were cut parallel to selected crystallographic planes using a diamond section machine and a Laue back-reflection camera for alignment. The thin sections were polished on diamond impregnated laps. Laue back-reflection photographs of the crystals and polished thin section exhibited sharp diffraction spots and no indications of the presence of more than one phase. Portions of the polished thin sections were powdered and used in the lattice constant determinations, wet chemical analysis and NGR measurements. Lattice constants were determined using a powder diffractometer and Mn filtered, Fe Kα radiation and a silicon internal standard.

The ^{57}Fe NGR measurements were performed on a constant acceleration spectrometer with an electromechanical velocity transducer and a 512 channel multichannel analyser operated in the multi-scaling mode. A 25 mCi Co^{57}/Rh source was employed, and Fe metal and sodium nitroprusside were used to calibrate the spectrometer. The Néel temperatures were determined using the thermal scanning NGR technique.[7] The Néel temperatures have an estimated error of ±5 K. The NGR applied field spectra were obtained in a superconducting solenoid in which the source and absorber temperature were separately controlled with a temperature stability of 1 K. Platinum resistor thermometer and an iron-constantan thermocouple were used for temperature control in the Néel temperature determinations and semiconductor diodes were used for temperature control during the applied field measurements. The NGR absorbers were in the form of thin discs prepared from acetone/Duco cement slurries of the powdered thin sections and were either mounted on mylar films or held between rigid boron nitride wafers.

RESULTS

The lattice constants and chemical compositions of the samples are listed in Table I. The ^{57}Fe NGR spectra at 298 K and at 50 K in an applied magnetic field of 50 kG are shown in Figs. 1, 2 and 3. The solid lines are the results of fitting the data points by a least-mean-squares technique to a number of different Lorentzian lines. The strong structure in the residual of the fit of two Lorentzian lines to the spectrum in Fig. 1. shows this fit to be unsatisfactory; the presence of at least one other quadrupole doublet is indicated. Several fits of two quadrupole doublets were attempted and the resulting parameters were observed to approximate those of $ZnFe_2O_4$[8] and $MnFeO_4$[9] at 298 K. The spectra of the low Mn^{3+} samples were therefore fitted to two quadrupole doublets with quadrupole splittings (ΔE_Q) and isomer shifts (δ) constrained to those of pure $ZnFe_2O_4$ and $MnFe_2O_4$, e.g., $\Delta E_Q = 0.58$ and $\delta = 0.31$ for $MnFe_2O_4$ and $\Delta E_Q = 0.35$ and $\delta = 0.37$ for $ZnFe_2O_4$. The intensities were free variables. The Chi-square of this fit was as small as or smaller than that of any other fit that corresponded to physically reasonable models of possible crystal chemistries. Especially noteworthy in Table I is the larger asymmetries in the areas of the two apparent lines for low Mn^{3+} samples compared to the high Mn^{3+} samples.

If the sample used to obtain the spectrum in Fig. 1 is annealed under vacuum at 600°C for 12 hours, the spectrum shown in Fig. 2 is obtained. It is obvious from the residual, the asymmetry in the line is much reduced; and the area ratio is observed to increase from 0.808 to 0.864.

At 77 K, the spectrum of all of the samples are qualitatively similar consisting of a broad apparent six line pattern. The average magnetic hyperfine field (H_{eff}) for sample 3, $Mn_{.487}Zn_{.699}Fe_{1.814}O_4$ in the absence of an applied field is 497 kG; in a 50 kG field at 50 K, the spectrum shown in Fig. 3 is obtained and two patterns are observed. One pattern is rather broad and has the smaller splitting corresponding to H_{eff} of 343 kG and the more widely split, sharper pattern has a H_{eff} of 467 kG. Both H_{eff} values are reduced below the zero-field values indicating that all Fe ions are on the B site and that the sample is ferrimagnetic. Fig. 3 is typical of the spectrum obtained for all samples but the relative widths and intensities of the lines of the two subspectrum varied considerably from sample to sample. For the low Mn^{3+} samples in the 50 kG applied field, the area ratios of the subspectrum with the large splitting to that with the smaller splitting were observed to be quite similar to the ratio of the areas of $MnFe_2O_4$ pattern to $ZnFe_2O_4$ pattern in the 298 K paramagnetic spectra; for example $A_{MnFe_2O_4}/A_{ZnFe_2O_4} = 0.32$ at 298°K and large$_{(large\ H_{eff})}$

$A_{(small\ H_{eff})} = 0.59 \pm 0.1$ at 50 K in a 50 kG field. This was not true of the high Mn^{3+} samples.

DISCUSSION

The presence of two patterns in the 298 K spectra of the low Mn^{3+} franklinites with ^{57}Fe NGR parameters appropriate to those of pure $ZnFe_2O_4$ and $MnFe_2O_4$ is interpreted as indicating the existence of two different regions in these samples having the corresponding compositions and local structures. The area ratio of the two doublets, $A_{MnFe_2O_4}/A_{ZnFe_2O_4}$ of 0.32 for $Mn_{.347}Zn_{.730}Fe_{1.923}O_4$ is very close to the Mn-Zn A site occupancy ratio of 0.37, indicating a high degree of ordering. That some kind of ordering is indeed present is confirmed by the change in the spectrum upon annealing the sample in the laboratory. Further direct evidence is provided by the low temperature applied field spectra in which the area ratios and relative magnitudes of the hyperfine fields are those expected on the basis of the 298 K spectra. Indirect evidence is provided by the value of the Néel temperature which is considerably lower than that of synthetic ferrites with similar compositions[10], and by the fact that upon annealing, the Néel temperature increases from 178 K to 233 K. A low Néel temperature and an increase in T_N upon annealing are in accord with the preposed structural and chemical ordering.

Although the Mn^{3+} content of these samples never reach the critical value necessary to cause cooperative Jahn-Teller distortions of the lattice, there are sufficient uncertainties in the magnitude and direction of the individual Jahn-Teller distortions such that samples with $Mn^{3+} > 0.08$ do not exhibit local structure comparable to those with the pure materials $ZnFe_2O_4$ and $MnFe_2O_4$. Thus, samples with the higher Mn^{3+} content are not susceptible to this type of analysis.

CONCLUSION

Unfortunately, naturally occurring ferrites similar to the samples studied in this paper would have little industrial importance, particularly with Néel temperatures of approximately 178 K. However, they served to demonstrate the presence of intrasite cation ordering and clustering in the less favorable case of the A sites, which share no polyhedral elements and are completely separated and therefore make plausible the existence of clustering and intrasite ordering on the B sites where electrostatic and structural factors provide stronger driving forces for ordering and clustering. Local ordering and clustering on the B sites are, however, difficult to demonstrate directly. Indeed, the present study provides direct and unambiguous evidence only for A site ordering and clustering but the A site order is so high that there must surely be some B site ordering. This ordering observed in these ferrites provide excellent opportunities for studies such as the effects of chemical inhomogeneities on reverse domain nucleation, B-H loop squareness and other magnetic properties. These studies also show that naturally occurring materials can be uniquely useful in magneto-crystal chemical studies of ferrites.

	COMPOSITION	LATTICE a_o (nm)	δ^a mm s^{-1}	ΔE_Q mm s^{-1}	DOUBLET AREA RATIO
1	$(Zn_{.730}Mn_{.270})\ [Mn_{.076}Fe_{1.924}]\ O_4$	0.8451	0.369	0.435	0.808
2	$(Zn_{.721}Mn_{.279})\ [Mn_{.040}Fe_{1.960}]\ O_4$	0.8457	0.365	0.420	0.915
3	$(Zn_{.699}Mn_{.301})\ [Mn_{.186}Fe_{1.814}]\ O_4$	0.8447	0.364	0.459	0.929
4	$(Zn_{.678}Mn_{.322})\ [Mn_{.570}Fe_{1.430}]\ O_4$	0.8476	0.367	0.471	0.903
5	$(Zn_{.665}Mn_{.335})\ [Mn_{.187}Fe_{1.813}]\ O_4$	0.8469	0.368	0.435	0.914

^{a}Relative to an Fe metal absorber

Table I Composition, lattice constants, and single quadrupole doublet ^{57}Fe NGR parameters of Zn-Mn-Ferrites at 298 K.

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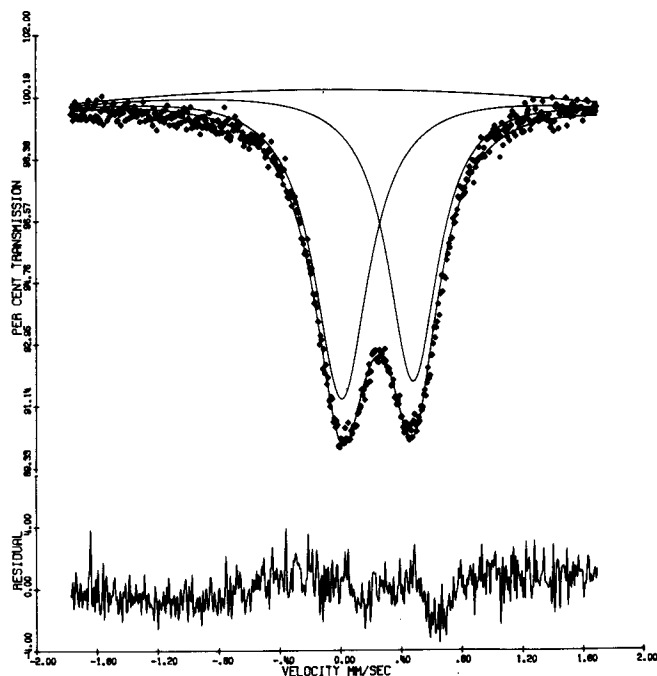10. Vogler, G., Phys. Stat. Sol. (b) 43, K161 (1971).

Fig. 2 ^{57}Fe NGR spectrum of sample in Fig. 1 after annealing at 600 C, under vacuum, for 12 hours. The solid line is the result of fitting two Lorentzian shaped lines to the spectrum. Note the much weaker structure in the residual.
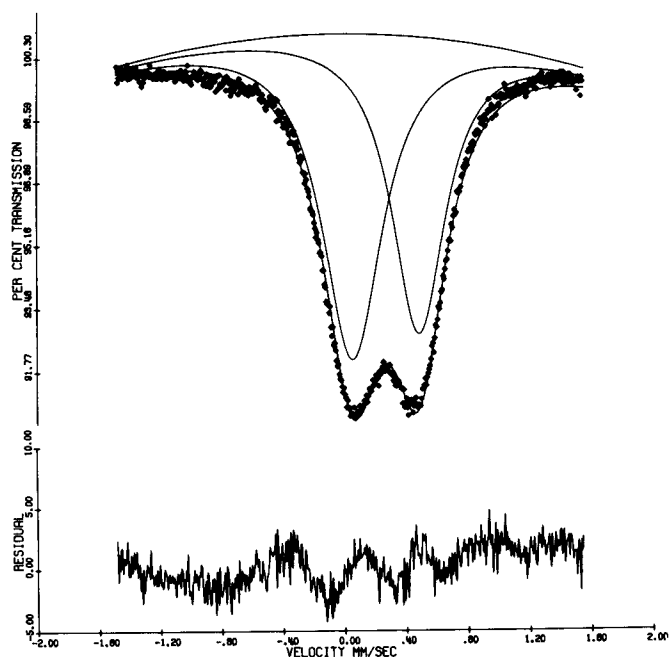

Fig. 1 ^{57}Fe NGR spectrum of $Mn_{.346}Zn_{.730}$ $Fe_{1.924}O_4$ at 298 K. Solid line is a result of fitting two Lorentzian-shaped lines to the spectrum. Note the strong structure in the residual.
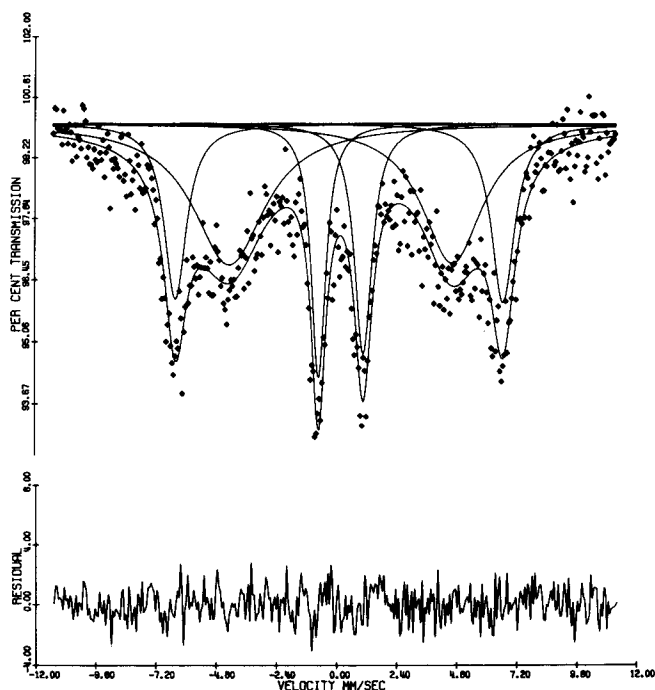

Fig 3 ^{57}Fe NGR spectrum of $Mn_{.319}Zn_{.721}Fe_{1.960}O_4$ at 50 K in a 50 kG applied field. The solid line is the result of fitting two 4-line patterns to the spectrum. Note the absence of the $\Delta M=0$ lines and the absence of any structure in the residual.