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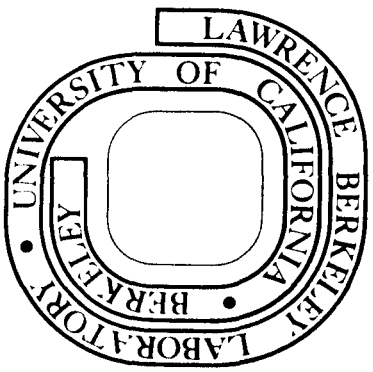

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MICROSTRUCTURE AND MAGNETIC PROPERTIES OF SPINEL FERRITES

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ABSTRACT

Achieving suitable magnetic properties in ceramic ferrites through thermomechanical treatments rather than through varying the processing and fabrication parameters alone are investigated. The high temperature phase transformation in lithium ferrite ($LiFe_5O_8$) spinel and the defects in $LiFe_5O_8$ and $NiFe_2O_4$ are studied using high voltage transmission electron microscopy in an effort to characterize the microstructures. Results show that a dispersion of paramagnetic $LiFeO_2$ particles in $LiFe_5O_8$ matrix gives rise to increased squareness of the hysteresis curve and increased coercivity. Annealing treatments of sintered ferrites remove undesirable intra-granular $\{100\}\frac{1}{4}\langle 110\rangle$ cation stacking faults and improve hysteresis loop parameters.

INTRODUCTION

The microstructure-sensitive magnetic properties of commercially used spinel ferrites are conventionally controlled by varying processing parameters[1] so as to change porosity, grain size, grain distribution etc. On the other hand, great success has been made in designing of metallic alloys for mechanical and physical applications through thermomechanical treatments to obtain sutiable microstructures. This has been possible solely due to our understanding of the microstructural features, (such as defects and phases) and their effects on the material properties[2] An analogous situation does not exist for ceramic materials, specifically because of the lack of detailed microstructural information on many ceramic systems. Recent developments of experimental tools such as high voltage transmission electron microscopy and ion-bombardment technique[3] for thinning non-metallic specimens have opened up the field of microstructural charactaerization in ceramic systems. In the present work, a high voltage electron microscopy study of microstructures in lithium ferrite and nickel ferrite has been carried out. The effect of these microstructures on the magnetic hysteresis curve has been studied. The significance and importance of these preliminary observations are discussed.

EXPERIMENT

High temperature phase transformations in lithium ferrite are studied by heating thin discs of $LiFe_5O_8$ single crystal in air, vacuum (10^{-5} torr) and oxygen (760 torr) at 1200°C for different lengths of time. Thin foil specimens for examination in the microscope are prepared from the center of these discs by mechanical polishing fcllowed by ion bombardment. Defects in single crystal lithium ferrite and polycrystalline nickel ferrite are studied by preparing thin foils from as-received as well as annealed materials. The electron microscope observations are made in a Hitachi Hu-650 high voltage electron microscope operating at 650 kV. The dynamic hystersis loops are taken at 60Hz using torroidal specimens. The size of the specimens used is 1 cm O. D., 0.6 cm I.D. and 0.2 cm thick. Twenty turns of copper magnetic wire are used in both primary and secondary windings.

RESULTS AND INTERPRETATION

A. Phase transformation and magnetic properties:

The phase transformation in air is described below in detail since air is the most economical atmosphere to maintain during any thermomechanical treatment. The features of the transformation are similar in other atmospheres. However, the transformation kinetics are quite different. The reaction proceeds faster in vacuum and slower in oxygen than in air.

On heating a 2mm thick disc of $LiFe_5O_8$ in air at 1200°C for about 25 minutes, one sees small octahedral shaped particles of a second phase homogenously dispersed as shown in Fig. 1a. The particles are of $LiFeO_2$ phase with a lattice parameter roughly half of that of spinel. Particles with an average size of 2500Å or less remain coherent with the matrix. Dislocation networks form at the interface to relieve the strain as the praticles grow larger.

Figure 1b shows the interfacial dislocations of Burgers vector $\frac{1}{2}\langle 110\rangle$ at the $LiFeO_2$-$LiFe_5O_8$ interface. Measurement shows that approximeately 10% of the spinel transforms to $LiFeO_2$. This $LiFeO_2$ later transforms to a lithium deficient spinel structure leaving behind incoherent grain-boundaries as in Fig. 1c.

The hysteresis loops corresponding to microstructures in Fig. 1a-c are given in Fig. 2a-c and Fig. 2d is the hysteresis curve for the as-received single phase material. The coercivity of the two phase microstructures in Fig. 2a or 2b is higher than that of single

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phase $LiFe_5O_8$. Also coercivity of polygranular single phase spinel as in Fig. 1c is higher than that of single phase crystal. $LiFeO_2$ phase is paramagnetic[4] and thus it is not surprising that its dispersion in a ferrimagnetic phase increases H_c by acting as a barrier to the domain wall motion[5]. Quantitative investigation of the dependence of H_c on particle size, volume fraction and coherency strain are in progress to verify Haasen's results.[5] A new and significant observation in Fig. 2 is that the squareness of the hysteresis loop, defined as $Br/4\pi M_s$) is higher for the two phase microstructures of $LiFeO_2$-$LiFe_5O_8$. Reduction of the value of M_s in Fig. 2c is due to reduction of Fe^{+3} to Fe^{+2}.

B. Defects and magnetic hysteresis:

Figure 3a shows the cation stacking faults in a specimen prepared from the vicinity of the surface of flux-grown $LiFe_5O_8$ single crystal. The faults are on {110} planes with $\frac{1}{4}\langle 110\rangle$ as the displacement vector[6]. The defect density decreases rapidly with increasing distance from the surface. The hysteresis loops of faulted and unfaulted materials are shown in Fig. 4. Presence of faults increases the coercivity. In the absence of any data on the magnetic domain configurations, a discussion on the interaction of the cation faults with the domains is not possible at this stage. It may be noticed that the M_s value of faulted and unfaulted materials are the same. Figure 5 shows a faulted grain in a polycrystalline $NiFe_2O_4$. More than 30% of the grains are seen to be faulted in the as-received crystals. On annealing the material in air for 12 hours at 850°C, the fault density decreases considerably, leaving about 95% of the grains fault-free with no other microstructural modifications. There is a change in the hysteresis curve as in Fig. 6.

DISCUSSION

Applications of ferrites in computer memory cores and in microwave device components such as latching devices[7] require good squareness of the B-H loop. A necessary condition for good squareness is the

dominance of the anisotropy energy over the magnetostrictive energy and this dictates the choice of materials. Proper processing is also used to enhance this effect[8]. The present results suggest yet another way of achieving it. In the absence of data on other magnetic properties of the two-phase systems, evaluation of the usefulness of these materials compared to the currently used ones is not possible, but it seems to be a step in the right direction in materials technology.

The result that H_c increases in a two-phase microstructure is not new[9], but the approach is new for ceramic magnets. It may be possible to use a similar approach to achieve better properties in hard magnetic ferrites than presently exist.

The polycrystalline nickel ferrites in the as-fabricated state are highly defective and this may be the reason for the poor performance of this material. (The samples examined here were from a rejected batch of commercial $NiFe_2O_4$ manufactured by Countis Industries, San Luis Obispo, California). All the magnetic properties of the annealed material have not been studied yet, but the data presented here suggests that a proper post-processing thermomechanical treatment may provide ways of improving the properties; thus reducing waste of material.

In conclusion, this preliminary study of the effect of microstructure on magnetic hysteresis shows that proper thermomechanical treatment of ceramic ferrites may be the step beyond the presently existing processes[1] which will bring about cheaper, better and more useful ceramic ferrites.

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* This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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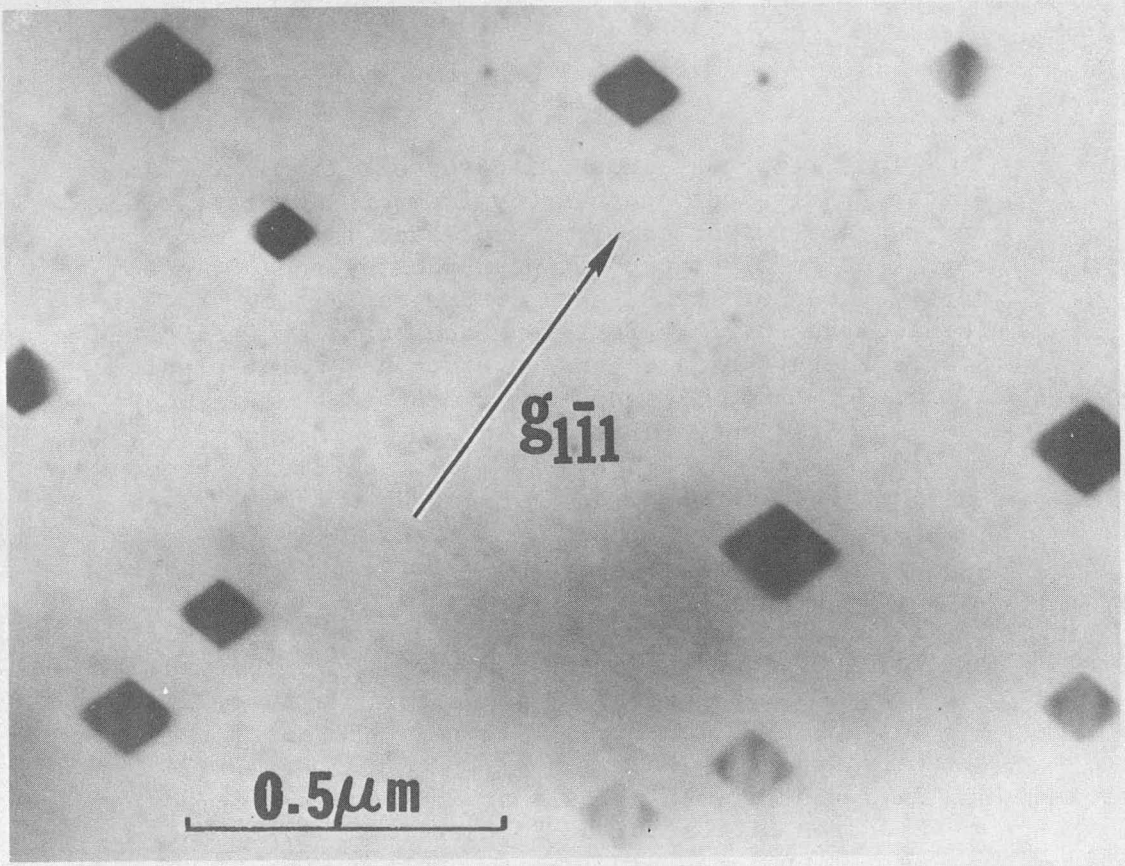

Fig. 1(a) Octahedral coherent precipitates of $LiFeO_2$ dispersed in $LiFeO_8$.

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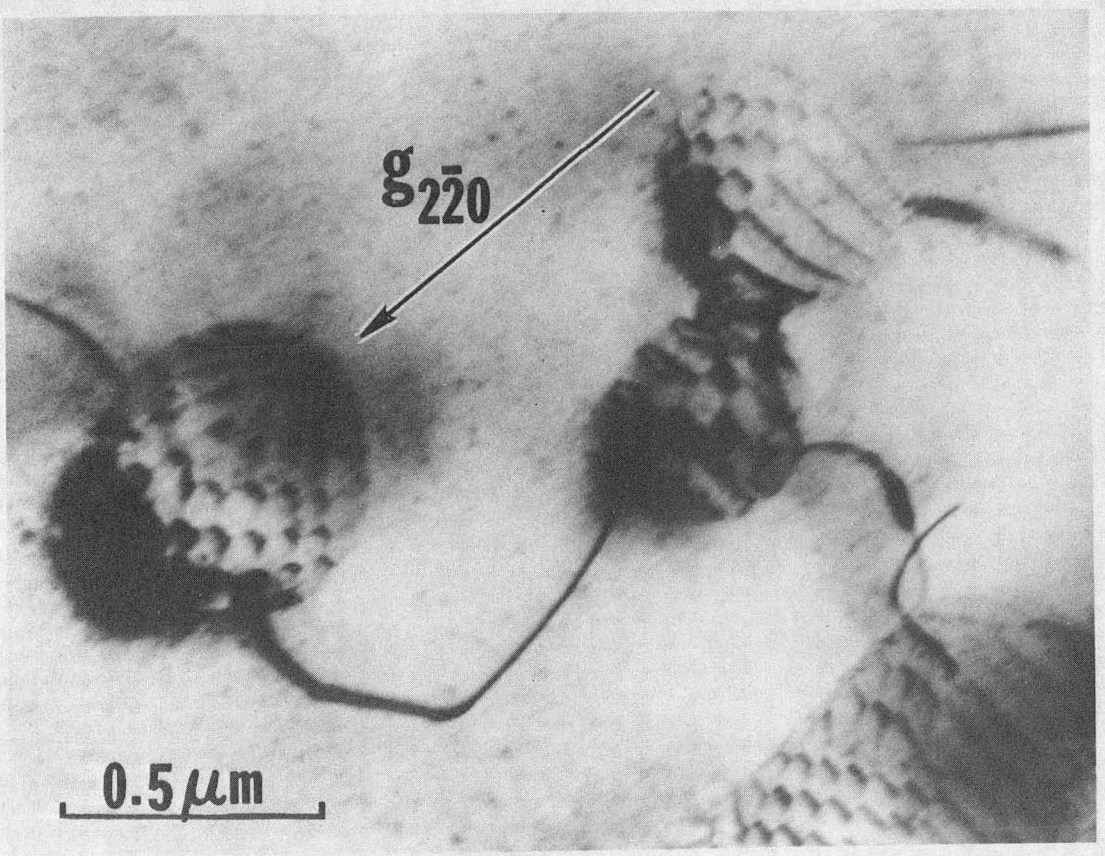

Fig. 1(b) Semicoherent $LiFeO_2$ particles with interfacial dislocations of Burgers vector $\frac{1}{2}\langle 110 \rangle$.

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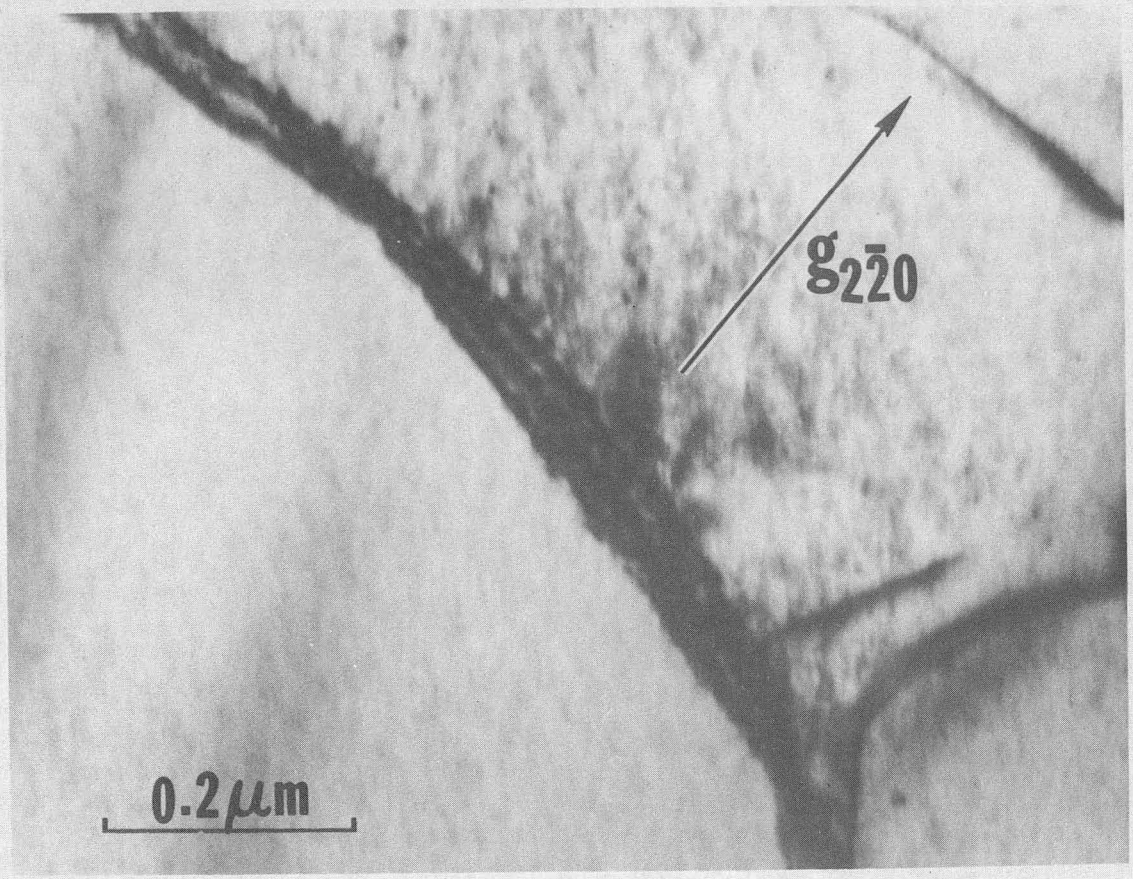

Fig. 1(c) Incoherent grain boundaries in the transformed spinel.

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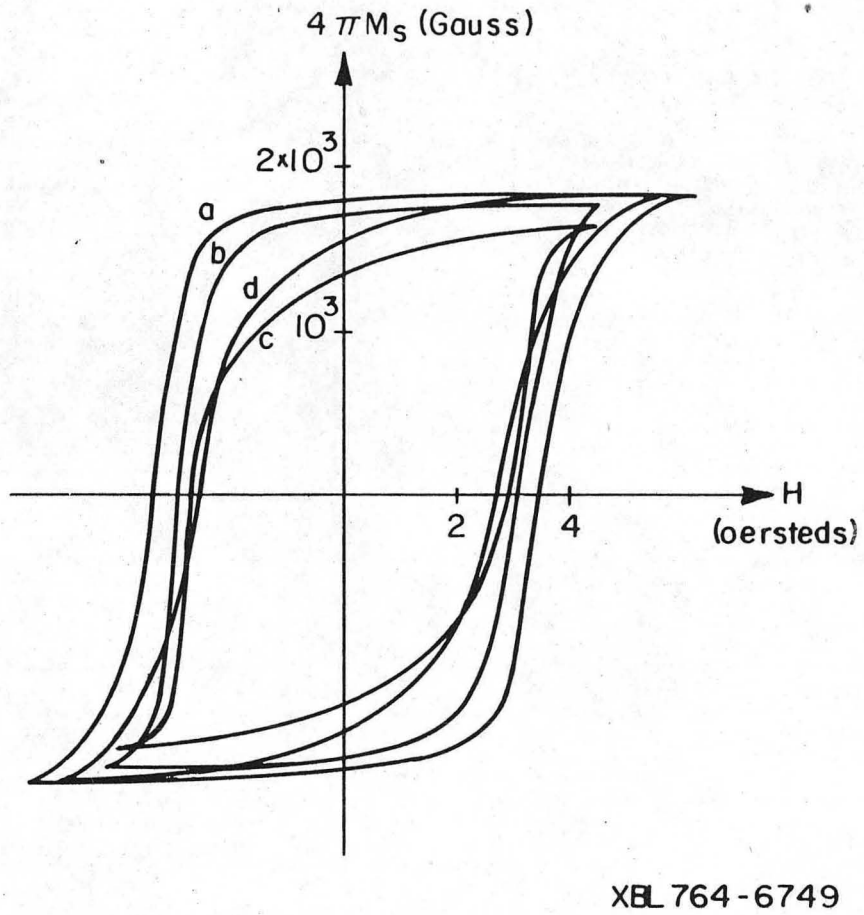

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Fig. 2 (a-c) Hysteresis loops corresponding to the microstructures in Fig. 1(a-c). (d) Hysteresis loop of the single phase $LiFe_5O_8$ single crystal.

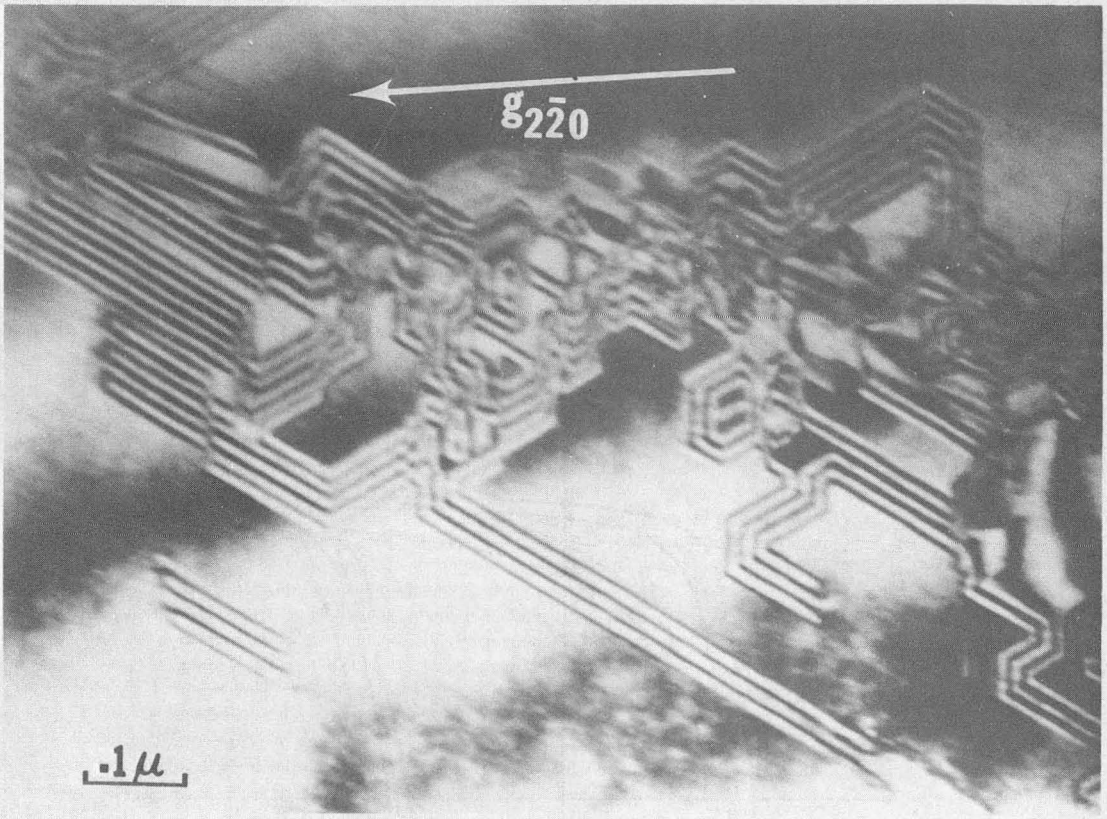

Fig. 3 Cation stacking faults in $LiFe_5O_8$. Faults lie on {110} planes with ¼<110> displacement vectors.

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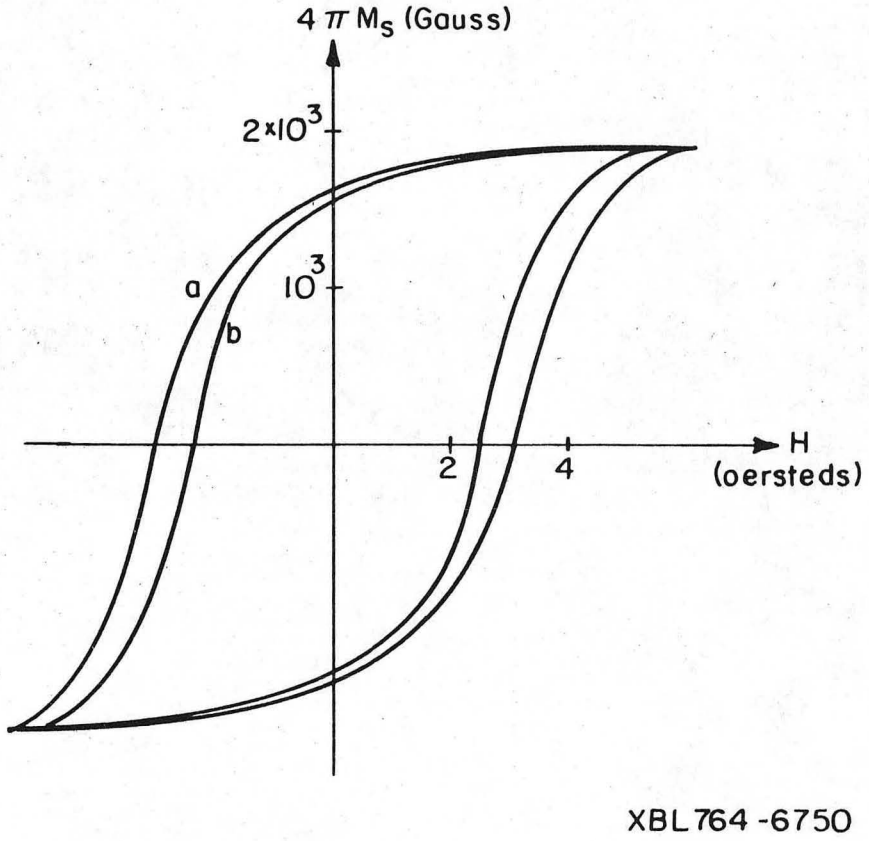

Fig. 4(a) Hysteresis loop corresponding to the microstructure in Fig. 3. (b) Same as Fig. 2(d).

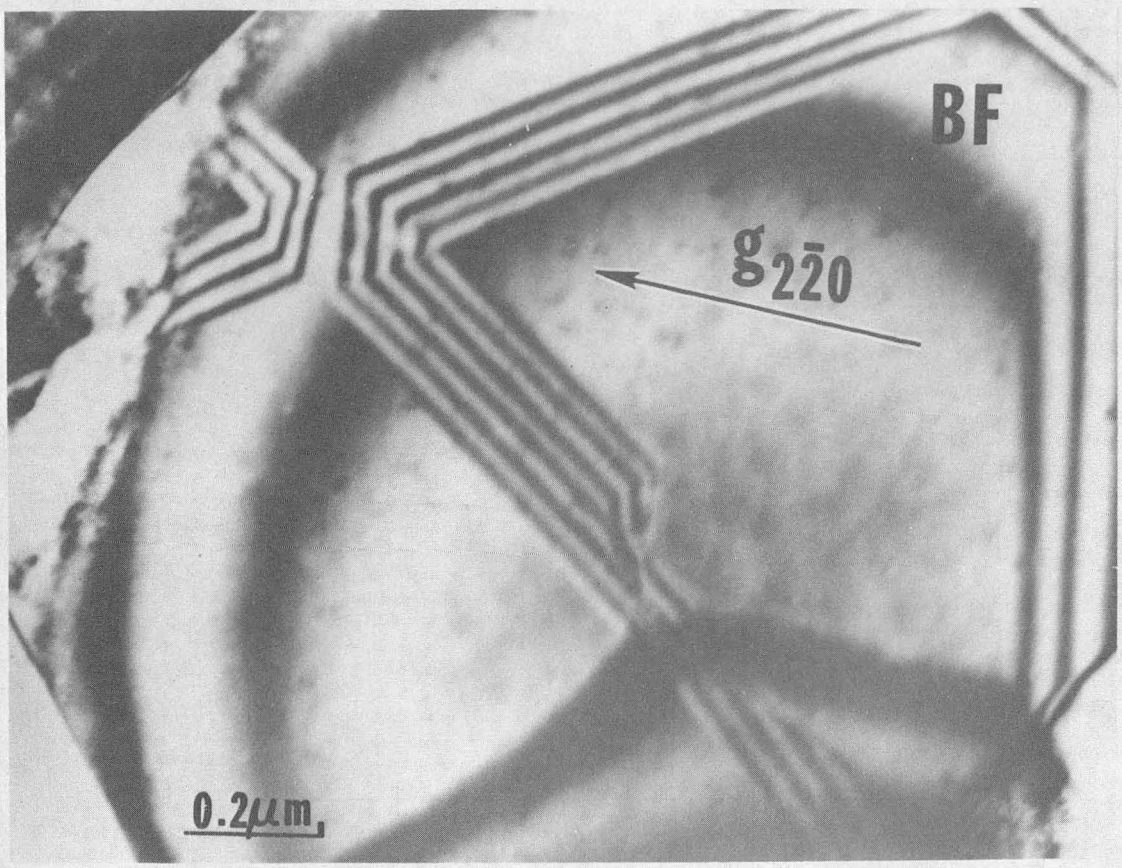

Fig. 5 $\{110\}\frac{1}{4}\langle 110\rangle$ cation fault inside a grain in polycrystalline $NiFe_2O_4$. Grain size is approximately 1.5 microns.

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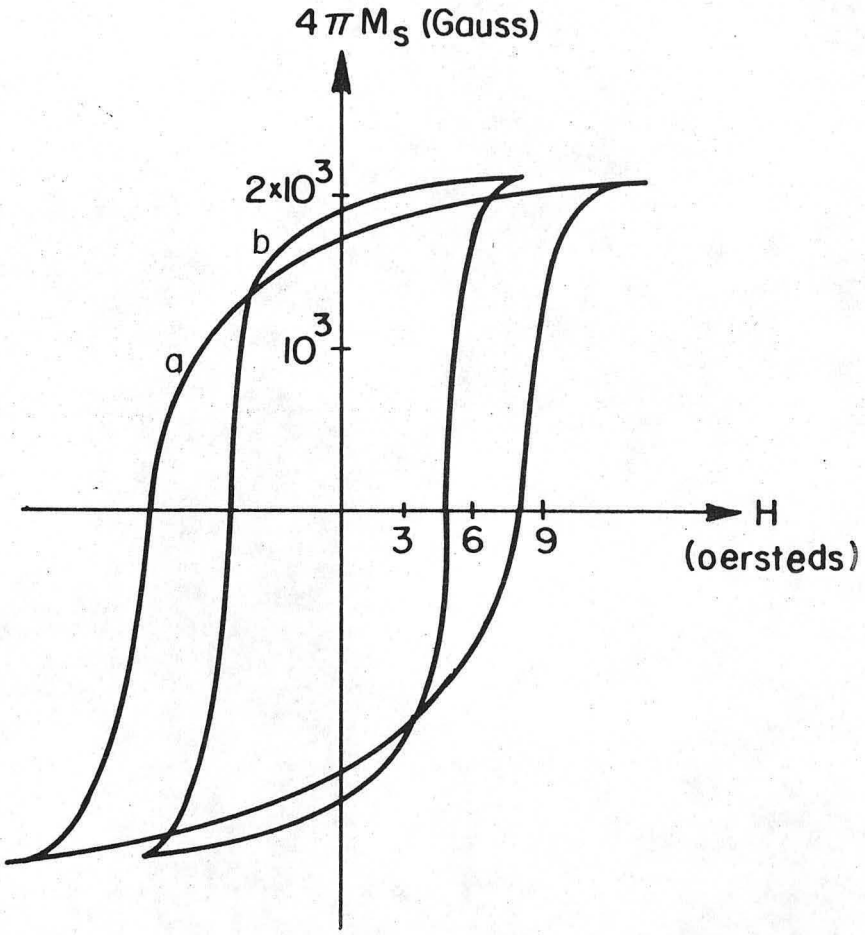

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Fig. 6(a) Hysteresis loop corresponding to microstructure in Fig. 5. (b) Hysteresis loop on annealing $NiFe_2O_4$ for 12 hrs at 850°C in air.

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