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LATTICE DEFECTS IN LITHIUM FERRITE SPINEL

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ABSTRACT

Structural defects in as-prepared and deformed lithium ferrite spinel are studied using transmission electron microscopy. Growth type cation stacking faults and glissile dislocation on \{110\} planes are observed. From the measured value of the spacing between the partials \( \frac{1}{2} \langle 110 \rangle = \frac{1}{4} \langle 110 \rangle + \frac{1}{4} \langle 110 \rangle \), the cation stacking fault energy is estimated to be about 75 ergs/cm\(^2\).

INTRODUCTION

It is now accepted that if both process route-structures and structure-property relationships can be established, together they provide a firm basis for the control and development of materials properties. The primary role of microstructural characterization in development work is the specification of structures to optimise process route-property relationships. Such basic studies are necessary for more efficient utilization of available materials and development of newer ones at a time when we face a resources crisis. With the advent of ion thinning techniques to prepare electron transparent foils from ceramic materials, and high voltage electron microscopes to examine thicker specimens with less damage due to ionization, the study of microstructures in ceramic materials is now receiving considerably more attention than a decade ago (e.g. refs. 1-3).

Structural defects are an important feature of the microstructure and their effects on the properties of ceramic materials can hardly be overemphasized e.g. magnetic characteristics of spinels\(^4\),\(^5\). The present paper deals with the characterization of defects found in, and produced during the deformation of lithium ferrite spinel using high voltage electron microscopy.
Lithium ferrite is a soft ferrimagnetic material that finds application in microwave devices and computer memory cores. It has a spinel structure with oxygen atoms forming a close-packed cubic lattice and metal ions occupying the "spinel" octahedral sites occupied randomly with Fe$^{+3}$ and Li$^+$ ions, i.e. an inverse spinel. The possible slip planes and slip vectors in the spinel structure have been discussed by Hornstra. With the requirement of electroneutrality through a synchroshear mechanism, Hornstra predicted that slip should occur on \{111\} planes in spinels, with a $\langle110\rangle$ as the slip vector. Experimentally, this prediction has been confirmed; and, in addition, other slip systems have been reported. Also, growth type stacking faults have been observed on \{100\} and \{110\} planes and twins, on \{111\} planes; but an understanding of these observations has not emerged yet. An explanation of the occurrence of the defects as observed in the present work and in those reported previously is presented.

**EXPERIMENTAL**

The single crystal of LiFe$_5$O$_8$ used in this study were obtained from Airtron-Litton Industries. Fifteen mil. thick discs with face normal along $\langle110\rangle$ were cut from the bulk single crystals using a diamond saw. These discs were deformed by a 3 point bending method at 1200°C in a vertical furnace. Thin specimens for examination in the electron microscope were prepared from the deformed and the undeformed crystals by cutting 3mm discs followed by subsequent mechanical polishing and ion-thinning. Thin foils were examined in a Hitachi Hu-650 high voltage electron microscope operating at 650 kV. The optimum conditions for high voltage microscopy analysis of defects was utilized as discussed elsewhere.

**RESULTS AND INTERPRETATION**

Figure 1 shows a stacking fault imaged in five different diffraction conditions. The faults can be characterised as follows: When the phase angle of the fault $\alpha = 2n\pi$, $\vec{R}$ is zero or an integral multiple of 2, the fault is invisible. Let the fault vector $\vec{R} = [hkl]$; then, from Figures 1(c), (e) and (f):

$$h-3k+l = n_1$$
$$-h+k+l = n_2$$
$$4l = n_3$$

where $n_1$, $n_2$, $n_3$ are zero or integers. Solving the three simultaneous equations;

$$h = \frac{1}{2}(n_3-n_1-3n_2)$$
With the choice of $n_1 = 1$, $n_2 = 0$, $n_3 = 1$, we find the smallest possible value of $R = \pm \frac{1}{4}[011]$. This is not a lattice vector but is the displacement vector of the fault lying on (011) as determined from trace analysis. By setting $\alpha = 2\pi g \cdot R = \pm \pi$ and the fringes show typical $\pi$ contrast (Fig. 1). The fault is bounded at its edges by sessile partial dislocations of Burgers vector $\frac{1}{4}[011]$, and corresponds to a stacking fault in the cation sublattice of the spinel as discussed by Van der Biest and Thomas. From image contrast analysis, however, it is not possible to distinguish between extrinsic and intrinsic $\pi$-faults in this material (i.e., whether material has locally been "removed" or "inserted" from the structure) and techniques such as direct lattice imaging may be necessary to establish this aspect of the fault. By comparing Figs. 1(c) and (f) it can be seen that the dislocation image widths are decreased by imaging in high order bright-field conditions (f) (see ref. 15).

Figure 2 is a high order bright-field image of dislocations in the deformed material. The dislocation density is not very high; however, straight dislocations lying parallel to the intersection of the foil plane (110) and other (110) planes can be seen. This indicates that slip (or recovery) has occurred on (110) planes. Healed cracks such as those in Fig. 3 are also seen occasionally in the deformed microstructure indicating that the material is not completely ductile at 1200°C.

Figure 4 shows a weak beam image of a dislocation network in deformed lithium ferrite. The dislocations lie parallel to the intersections of the other (110) planes with the foil plane and are dissociated into partials. The dissociation can be resolved to be

$$\frac{1}{2}[110] = \frac{1}{2}[110] + \frac{1}{2}[110]$$

on (110) slip planes. The image profile computed for the operating multibeam reflection conditions is shown in Fig. 4(c), which compares very well with the microdensitometer trace given in Fig. 4(b). The partials in the foil are separated by about 220Å. Using non-isotropic elasticity, it is calculated from this spacing that the surface energy between the partials i.e., the stacking fault energy is 75 ergs/cm². For an ionic solid such as LiFe₅O₈ spinel, this value seems to be low. Since it cannot be ascertained whether or not the partials are in equilibrium positions, as climb may occur during the high temperature deformation, this value of stacking fault energy, or surface energy, must only be approximate.

**DISCUSSION**

Experimental results show that growth type cation
faults occur on \{100\} and \{110\} planes in MgAl_2O_4 and on \{110\} planes in NiFe_2O_4, Fe_3O_4 and LiFe_5O_8. On the other hand, twinning occurs on \{111\} planes alone. Assuming a modified Coulomb interaction and Born Meyer repulsion between the ions and following a method of computation similar to that of Blandin, Friedel and Saada\textsuperscript{16}, the energies associated with planar defects on various planes can be calculated (details of the computation will be published elsewhere). These calculations show that, in fact, twins on \{111\} have energies much lower compared to those of the growth type cation stacking faults on \{111\} planes. Also, cation stacking faults should occur with higher probability on planes such as \{110\} and \{100\} than on \{111\} planes. As pointed out by Veyssiere et al.\textsuperscript{17}, such computations are significant only for comparison purposes and thus are only semiquantitative.

The original prediction of Hornstra\textsuperscript{7} about the fourfold dissociation of a dislocation on \{111\} planes has not been confirmed experimentally although images with four intensity peaks have been recorded under different diffracting conditions\textsuperscript{18}. One such example is shown in Fig. 5a. Fig. 5a is the weak beam image of a dissociated dislocation and the corresponding high order bright field image is shown in Fig. 5b. As can be seen, the high order bright field image does not show the extra intensity peaks present in the high resolution dark field image of Fig. 5a. It has been confirmed through computation of the image profiles that the extra intensity peaks in Fig. 5a are purely due to dynamical scattering effects and not to structural characteristics. Also, slip systems other than the ones predicted by Hornstra have been reported as in the present paper, and rather more frequently in nonstoichiometric spinels\textsuperscript{9}. Calculation of the Peierls' stress on different crystallographic planes remains to be done and the understanding of the slip system in spinels is far from clear. However, the present results show that dislocation motion in LiFe_5O_8 occurs on \{110\} planes alone, in spite of the fact that the Schmidt factor for \{110\}\textsubscript{4}<110> is less than that for \{111\}\textsubscript{4}<110> under the loading conditions.

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REFERENCES


Fig. 1. An isolated cation fault with $R = \frac{1}{2}[01\bar{1}]$ in LiFe$_5$O$_8$ imaged under different diffracting conditions. Note the symmetry of the π-fringes in the dark field image in (a) and the complementary nature of the bright field and dark field images in (a) and (b). The fault is out of contrast when $g.R = 0 \text{ or integral as in e or f and c, but the bounding partials } g.b = b.R = 0$. The width of the dislocation image in (f) is reduced when the 008 reflection is excited.

Fig. 2. High order bright field image of straight parallel dislocations with Burgers vector $\frac{1}{2}[01\bar{1}]$ lying in the plane of the foil, parallel to [\bar{1}11] direction which is the line of intersection of the (110) foil plane and the (011) slip plane.

Fig. 3. Bright field image of healed cracks in lithium ferrite spinel deformed at 1200°C.

Fig. 4. (a) High resolution dark field image of dissociated dislocation network in deformed lithium ferrite spinel, (b) microdensitometer trace at A in Fig. (a), (c) computed image profile for the dissociation $\frac{1}{2}[01\bar{1}] = \frac{1}{2}[01\bar{1}] + \frac{1}{2}[01\bar{1}]$ on (011) plane.

Fig. 5 (a) Weak beam image of a dissociated dislocation. The dissociation can be represented as $\frac{1}{2}[01\bar{1}] = \frac{1}{2}[01\bar{1}] + \frac{1}{2}[01\bar{1}]$, on the (011) plane. (b) High order bright field image of the same dislocation. Note the four intensity peaks in (a) due to dynamical scattering effects.
FIG. 3
FIG. 4
FIG. 5
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