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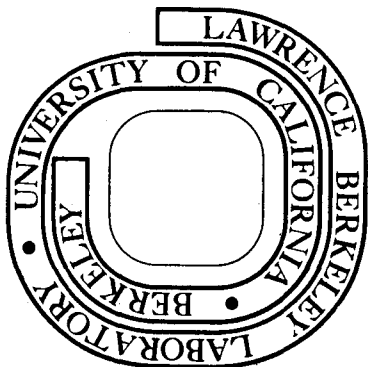
O. Van der Biest and G. Thomas

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THE ORDER-DISORDER REACTION IN LITHIUM FERRITE

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Lithium ferrite (LiFe_5O_8) is a ferrimagnetic ceramic with some interesting technological properties. It has an inverse spinel structure (general formula $\text{A B}_2\text{O}_4$) with Fe^{3+} on tetrahedrally coordinated sites (A-sites) and a 3:1 mixture of Fe^{3+} and Li^+ on the octahedral sites (B-sites). Below 750°C the cations are ordered. Some important properties of the material (e.g. the ferrimagnetic resonance linewidth (Denton and Spencer, 1962), and the d.c. electrical resistivity (Van Aulock, 1965), show a marked dependence on the degree of order. In this paper, the domain structure resulting from the order-disorder reaction will be described and some observations on the kinetics of the reaction will be presented.

When disordered lithium ferrite orders, its space group symmetry is lowered from $\text{Fd}\bar{3}\text{m}$ to $\text{P}4_1\bar{3}2$ or its enantiomorph $\text{P}4_3\bar{3}2$ (Braun, 1952). A projection of the configuration of the Li and Fe ions on the octahedral sites in both the lefthanded ($\text{P}4_3\bar{3}2$) and the righthanded arrangement is given in Figure 1. Within each spacegroup the ordered structure can be described as an alternation of three iron ions and one lithium ion along $\langle 110 \rangle$ rows. Hence, the set of octahedral sites can be divided into four subsets, one of which contains only lithium ions and the other three only iron ions. When ordering sets in, the lithium ions can occupy any of these four subsets. After ordering, the single crystal is fragmented into domains, in a way similar to that found in ordered metallic phases. Within each domain, the lithium ions will

occupy only one subset and at the boundary between domains they will be out of phase. These boundaries can be described by a $\frac{1}{2} \langle 110 \rangle$ type vector, which is a lattice vector of the disordered structure. Hence, a translation of the ordered structure over this vector does not affect the oxygen ions nor the iron ions on tetrahedral sites but it does transfer the Li ions from one subset to another. This holds for either one of the spacegroups. So there are actually eight different subsets out of the 16 octahedral sites which the Li ions can occupy and it is possible to have a boundary between any pair of these. One could have a total of 28 boundaries between the eight possible arrangements. However, only seven boundaries, distinct in the geometrical operations characterising them can occur. These are indicated schematically in Figure 2. The ordered variants 1L and 1R of Figure 2 are pictured in Figure 1. These have arbitrarily been chosen as "basic" arrangements for $P4_332$ and $P4_132$ respectively. The other arrangements are derived from these by a translation of the Li ions over a $\frac{1}{2} \langle 110 \rangle$ vector. The two "basic" arrangements can be brought into coincidence with one another by an inversion through the point $(5/8, 5/8, 5/8)$ and the boundary between these two will be called an inversion boundary. Among the seven possible boundaries indicated in Fig. 2, there are three translation boundaries, one inversion boundary and three boundaries described by an inversion and a translation.

Two different methods of analysis have been used to verify this domain structure (Van der Biest and Thomas, 1974): (i) the boundaries themselves can be imaged as α fringes (see Chapter 1) with $\alpha = 2\pi \bar{g} \cdot \bar{R}$

for translation boundaries. For the boundaries involving an inversion $\alpha = \alpha_g^l - \alpha_g^r$ where α_g^l and α_g^r are the phase angles in the structure factor expressions $F_g^l = |F_g^l| \exp(i\alpha_g^l)$, and $F_g^r = |F_g^r| \exp(i\alpha_g^r)$, calculated with respect to the same origin. The following table gives the value of α for the seven boundaries and some selected reflections:

g	T ₁	T ₂	T ₃	I	I+T ₁	I+T ₂	I+T ₃
0 $\bar{1}$ 2	π	0	π	$\pi/2$	$-\pi/2$	$\pi/2$	$-\pi/2$
$\bar{1}$ 10	0	π	π	π	π	0	0
0 $\bar{1}$ 1	π	π	0	π	0	0	π
$\bar{1}$ 01	π	0	π	π	0	π	0

(ii) In the second method, one takes advantage of the violations in Friedel's law in non-centrosymmetric crystals. This means that +g and -g do not have the same intensity even when the excitation errors are the same. At an inversion boundary, when +g is operating in one part of the crystal, -g is operating in the inverted part with exactly the same excitation. According to Serneels et al (1973) Friedel's law does not hold for the dark field in a multiple beam orientation when the crystal is oriented with the electron beam parallel with a zone axis along which the projected structure does not show an inversion point. Under these conditions one may expect differences in background intensity at a boundary where an inversion takes place. These two methods of analysis are used in Figure 3 to analyse the domains in the same area. In Figures 3a-3d, we have a two beam condition, or at least a systematic row of reflections is operating. The boundaries can be

identified from their visibility or invisibility in different diffraction conditions, using the table given above. The results are indicated in Fig. 3a, where the configuration of one domain was assumed. From the identifications of the boundaries, all the other domains can be labelled in a self consistent manner. Figures 3e and 3f were taken with the diffraction conditions shown in Figure 3g, and illustrate the second method of analysis. The fringes in Figure 3e, running from right to left are thickness fringes. They remain continuous across the boundaries in the bright field picture. In dark field, however, (Figure 3f), these fringes change contrast at some boundaries (e.g. at the boundaries marked a and c but remain continuous across others (e.g. at j and g). Comparison with Figure 3a shows that the latter ones are translation boundaries, whereas the first ones are inversion boundaries.

Figure 4 summarises a few results on the kinetics of the reaction. All specimens were annealed for 30 minutes at 950°C and subsequently water quenched. They were then annealed for various times: Figures 4a, 4b and 4c at 743°C for 1 minute, 10 minutes, 100 minutes respectively, figures 4d, 4e, 4f at 650°C for 1 minute, 10 minutes, 100 minutes respectively. At 743°C after 10 minutes (Fig. 4b) domains are nucleating in the disordered matrix. After 100 minutes (Fig. 4c) the reaction is still not complete as there is still some disordered material left. However, meanwhile the domains have substantially coarsened, as is evidenced by the large difference in number of particles per unit volume. At 650°C the formation of long range ordered domains is preceded by a substantial sharpening of the superlattice reflections (Fig. 4d)

-5-

although these remain much weaker than in the fully ordered structure. In the images domains are only clearly resolved after 10 minutes, e.g. in Figure 4c. Long range ordered domains have nucleated and grown till they touch each other and anti-phase domain boundaries have formed. After 100 minutes (Fig. 4f) the domains have coarsened through annihilation of anti-phase domain boundaries. A more detailed study of the kinetics of the reaction will be published shortly.

ACKNOWLEDGEMENTS

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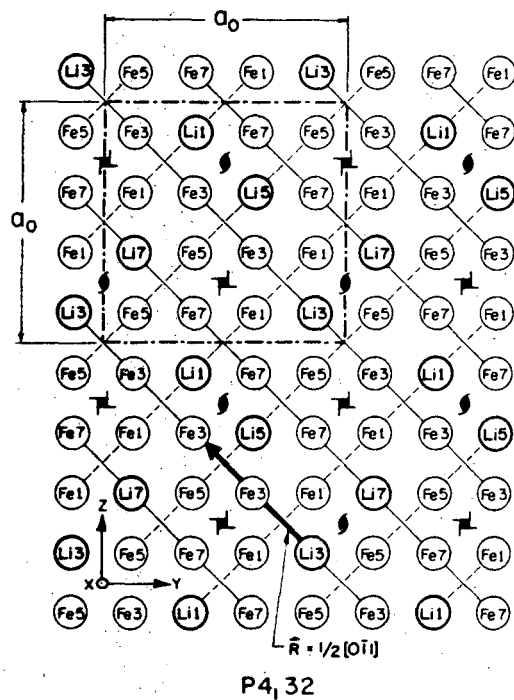
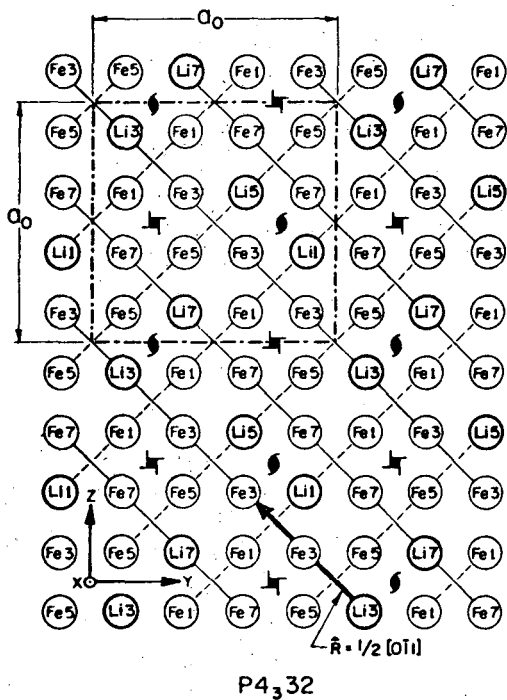
Serneels, R., Snykers, M., Delavignette P., Gevers R., and Amelinckx, S., "Friedel's Law in Electron Diffraction as Applied to the Study of Domain Structures in Non-centrosymmetrical Crystals", phys. stat. sol. 58 (b), 277-292, (1973).

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Von Aulock, W.H., Handbook of Microwave Ferrite Materials, Academic Press (1965).

FIGURE CAPTIONS

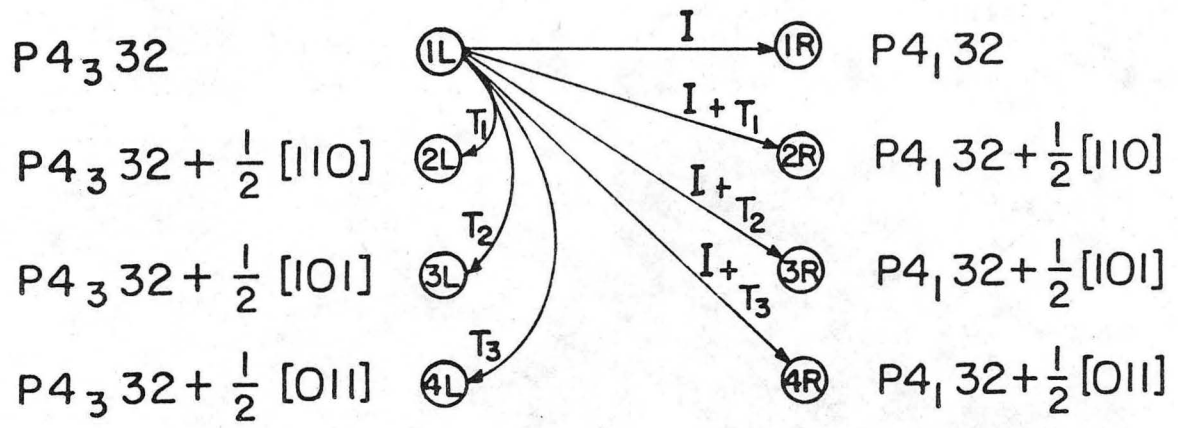
- Fig. 1: Projection of the two ordered variants on the (100) plane.
Only the octahedral sites are shown.
- Fig. 2: Schematic representation of the seven different boundaries in
ordered lithium ferrite.
- Fig. 3: An identical area in an ordered crystal photographed under
five different diffracting conditions.
- Fig. 4: Study of the kinetics of ordering in lithium ferrite.



$\textcircled{\text{Fe}}$ $\textcircled{\text{Li}}$ Fe or Li atom at a level $nz a_0/8$ above the plane of the paper

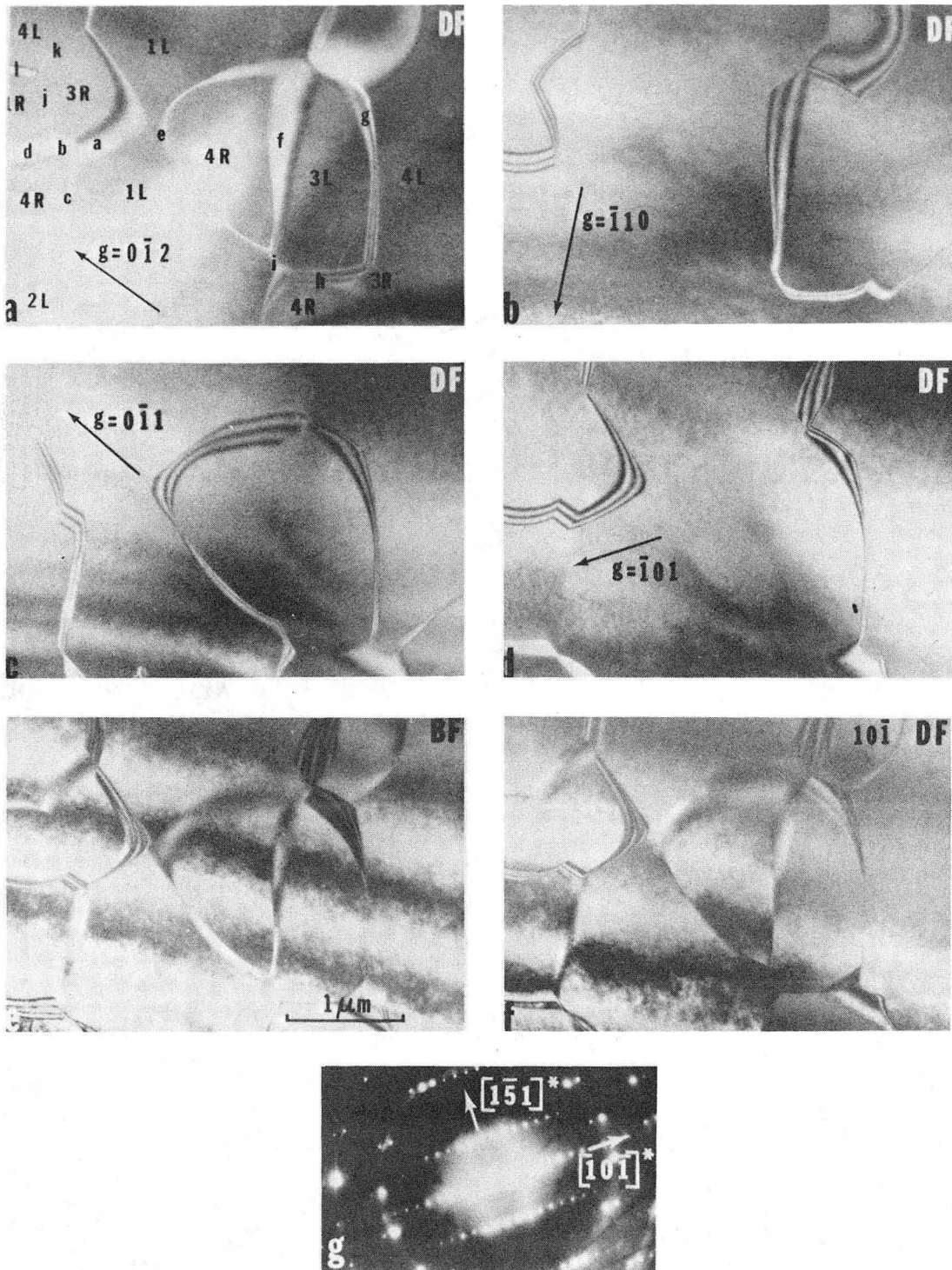
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FIG. 1



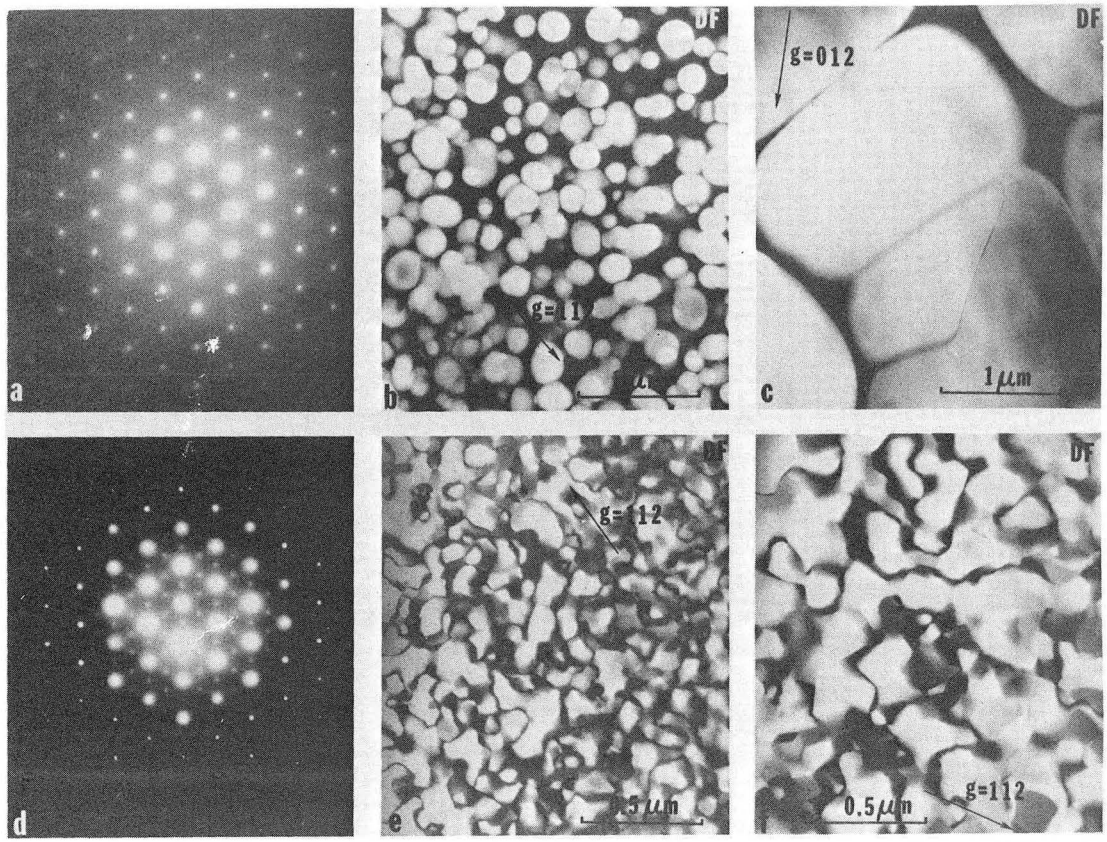
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FIG. 2



XBB 743-1710

FIG. 3



XBB 749-6510

FIG. 4

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