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Mishra, Raja K.

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MATERIAL LOSS AND HIGH TEMPERATURE PHASE TRANSITION
IN LITHIUM FERRITE

Raja K. Mishra*, Omer O. Van der Biest*
and G. Thomas*

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Engineering,
University of California, Berkeley, California 94720

ABSTRACT

The kinetics and crystallography of the phase transformation accompanying oxygen and lithium loss in $\text{LiFe}_{5/8}\text{O}_8$ have been studied at 1200°C in air, oxygen ($P_{\text{O}_2} = 760$ torr) and vacuum ($P = 5 \times 10^{-5}$ torr) using high voltage electron microscopy. LiFeO_2 was observed to nucleate and grow in the $\text{LiFe}_{5/8}\text{O}_8$ matrix, and finally transform to spinel in all three atmospheres; but the kinetics of the transformation depend on the atmosphere. It is concluded that the amorphous phase that forms in the flux grown single crystals and not in the polycrystalline $\text{LiFe}_{5/8}\text{O}_8$ is not intrinsic to the Li-Fe-O system.

*Member, the American Ceramic Society

I. INTRODUCTION

Lithium Ferrite is a ferrimagnetic material with many attractive properties⁽¹⁾. Its main asset is a high Curie temperature of about 650°C. With proper preparation, high electrical resistivity⁽²⁾, a square hysteresis loop⁽³⁾, a low resonance line width⁽⁴⁾ can also be obtained. These properties are however, strongly dependent on the history of the sample. It is generally assumed that this material loses appreciable amounts of oxygen and lithium above 1000°C where it would be desirable to sinter the material. It is this material loss that has limited the application of pure and doped lithium ferrites and hence the phenomenon has received the attention of a number of investigators⁽⁵⁻¹³⁾. In all these studies the authors have used powder compacts with Fe_2O_3 and Li_2CO_3 as starting materials, sometimes with LiFeO_2 as an intermediate product. The resulting powder compacts need to be prepared at low temperature, at times with the help of a packing powder⁽⁷⁾, in order to prevent material losses prior to the actual measurements. Hence these powder aggregates often contain traces of unreacted Fe_2O_3 and (or) LiFeO_2 . In addition, the study of the material loss in lithium ferrite is hampered by the following:

(i) Chemical analysis of lithium is difficult and expensive, (ii) Phase identification using X-ray diffraction is also difficult, especially the detection of small amounts (up to 20%) of the LiFeO_2 phase because its interplanar spacings are very close to those in LiFe_5O_8 so that the X-ray diffraction peaks overlap. Salmon and Marcus⁽¹¹⁾ postulated that LiFeO_2 could be formed as an intermediate phase during the decomposition of the spinel. Evidence for the occurrence of LiFeO_2 phase

near the surface of a sample with excess lithia, has been obtained by Bondyopadhyay and Fulrath⁽⁷⁾.

In the present work the high temperature material loss in lithium ferrite has been studied using single crystals, to ensure that the starting material is single phase. The microstructures resulting from the material loss have been characterised in detail using high voltage transmission electron microscopy. The kinetics and the mechanism of the phase transformations accompanying the material loss have also been studied.

II. EXPERIMENTAL PROCEDURE

Flux grown single crystals of lithium ferrite spinel with a maximum dimension of 2 cm were obtained from Airtron Litton Industries. These crystals contained particles of vitrified flux trapped during growth. The portion of the flux trapped in open pores could simply be removed by heating the crystal to 750°C, where these flux particles become liquid. Semi-quantitative spectrographic analysis of such a crystal is given in Table I. The flux contained PbO and B₂O₃; these oxides also showed up in the chemical analysis but some of it is due to the flux particles trapped in closed pores. Quantitative chemical analysis revealed that the crystals were slightly deficient in Li with a Fe/Li ratio of $5.17 \pm .27$ as determined by flame photometry. The starting material had a homogeneous single phase spinel microstructure as revealed by TEM. From X-ray measurements the lattice parameter was found to be 8.33 Å. The temperature of the heat treatments was kept constant at 1200°C for all runs. The effects of three atmospheres; air, 1 atm. O₂ and a vacuum of 5×10^{-5} torr were investigated. It was expected that

gradients in composition would occur throughout a crystal as oxygen and lithium were lost from the surface. Thin foils from different depths of the specimen were prepared to study the reaction sequence in the interior of the crystals. In order to follow the microstructural changes with annealing time, care was taken to prepare a sample for observation in the electron microscope at fixed distances from both surfaces of a thin slice of crystal. These slices were all ground to a thickness of 0.015 inch with faces nearly parallel to {110}. The slices were heat treated for different times (see Table II) in the three different atmospheres; care was taken that both faces were exposed to the environment during heat treatment. Specimens for electron microscopy were prepared from the heat treated samples by drilling a small disc from the center of the sample, mechanically polishing the disc to a thickness of 8 μ and finally by ion thinning.

Specimens prepared in this way exhibited some surface irregularities⁽¹⁴⁾, but all the artifacts due to the specimen preparation method could easily be identified since these were present in all specimens. All the microscopy was done using a HU-650 transmission electron microscope operating at 650 kV.

Some sintered polycrystalline samples were prepared starting from Li_2CO_3 and Fe_2O_3 (processing details can be found elsewhere)⁽⁷⁾. These were sliced and heat treated. Specimens prepared from them were examined in the microscope under the same conditions.

The iron and lithium contents in the annealed and unannealed samples were determined by semi-quantitative chemical analysis for a few specimens and are listed in Table III.

III. RESULTS AND INTERPRETATION

The mechanism of the phase transitions as observed in the HVEM are the same in air-annealed, vacuum annealed, and oxygen annealed samples. However, there are significant differences in the kinetics as revealed by a comparison of the observations on samples aged in air, oxygen and vacuum under otherwise identical conditions.

The results of the air-annealed single crystals are presented first, followed by a discussion of the additional features seen in the oxygen-annealed and vacuum annealed crystals. Results of the experiments on polycrystalline samples are then presented at the end of this section.

(a) Transformation in air:

Technologically air is the most important atmosphere during processing and hence our observations in air are discussed below in detail. For convenience, the sequence of events are discussed in terms of the three different stages of transformation, as shown schematically in Fig. 1.

(i) The early stage: (Stage I) This corresponds to the interval when precipitates of LiFeO_2 form. After 15 minutes, the microstructure near the center of the heat-treated discs consists of coherent octahedral shaped particles of LiFeO_2 dispersed randomly in the spinel matrix as shown in Fig. 2. Particles with an average dimension of $2500\text{\AA}$ or less remain coherent with the matrix. The precipitate-matrix interfaces are parallel to $\{111\}$ planes and there is negligible strain contrast around these particles.

The octahedral particles grow in size and become semicoherent with the matrix in regions nearer to the disc surface. The structure of the new phase is determined by examining the electron diffraction patterns from the precipitate and the matrix. Figure 3 shows the SAD patterns from a) matrix only, b) precipitate and matrix, c) precipitate only, and d) the $[110]$ reciprocal lattice sections of the precipitate and the matrix (including the spots that may arise due to double diffraction) superimposed on each other. The second order spots of the matrix coincide with the first order spots of the precipitate. The orientation relationship can be written as

$$\begin{aligned} (1\bar{1}0)_{\hat{m}} // (1\bar{1}0)_{\hat{p}} \\ [110]_{\hat{m}} // [110]_{\hat{p}}, [001]_{\hat{m}} // [001]_{\hat{p}}. \end{aligned}$$

i.e. perfect matching of parallel crystallographic planes and directions. BF and DF images taken from the first and second order spots of a $\langle 2\bar{2}0 \rangle$ systematic row are shown in Fig. 4. From the figure it is apparent that spot 1 on the systematic row arises from the matrix while spot 2 arises from both the matrix and the precipitate. This leads to the conclusion that the precipitate has a cubic structure with lattice parameter which is almost exactly half of that of the matrix. From X-ray measurements, the room temperature lattice parameter of LiFe_5O_8 spinel is $8.33 \text{ \AA}$. On the basis of ASTM data on $(\text{Li}, \text{Fe}, \text{O})$ compounds and the results of earlier investigations^(8,11), the new phase here is inferred to be lithium ferrate (LiFeO_2) with the rock-salt structure and a room temperature lattice parameter of $4.14 \text{ \AA}$. This result is further confirmed by the fact that diffuse scattering arising due to short range order in LiFeO_2 ⁽¹⁵⁾ precipitates is observed in Fig. 3c

and less clearly in Fig. 3b.

The growing precipitates have two different kinds of morphologies. Some precipitates are highly elongated while others remain nearly spherical. Figure 5a shows few isolated spherical precipitates which are semicoherent with the matrix and are connected by matrix dislocations. Precipitates nucleated heterogeneously on dislocations are shown in Fig. 5b. Fig. 5c shows an elongated precipitate resulting from the coalescence of these particles. Precipitates as long as 25μ have been observed compared to the lateral dimensions of about 1μ . Figure 6 shows part of an elongated precipitate in two different diffracting conditions. The semicoherent interface consists of a network of dislocations with Burgers vector $a/2 \langle 110 \rangle$. Dislocations visible in Fig. 6 a and b have $1/2[1\bar{1}0]$ and $1/2[101]$ Burgers vectors, and the average separations between the dislocations are $1100\text{\AA}$ and $640\text{\AA}$ respectively. Assuming the interface as fitting together of two crystals of slightly different lattice parameters but identical orientations, we may determine the misfit parameter δ from Brook's⁽¹⁶⁾ relation

$$\delta = \frac{2(a_1 - a_2)}{a_1 + a_2} = \frac{b}{D}$$

where b is the component of the Burgers vector in the plane of the interface, D is the average distance between dislocations and a_1, a_2 are the lattice parameters of the two crystals. For $D = 1100\text{\AA}$ and $\vec{b} = 1/2[110]$ for the edge dislocations on (110) as in Fig. 6a, $\delta = 5.4 \times 10^{-3}$. For $D = 640\text{\AA}$ and $1/2[001]$ as component of $\vec{b}$ on (110) along $[001]$ in Fig. 6b, $\delta = 6.5 \times 10^{-3}$. Thus the average value of δ as measured from the misfit dislocation spacings is 5.95×10^{-3}

which compares very well with the value of δ obtained from the values of the lattice parameters of LiFeO_2 and $\text{LiFe}_{5/8}\text{O}_8$.

A rough estimate shows that the volume fraction of the LiFeO_2 is about 10-12%.

(ii) The Intermediate Stage (Stage II): With longer aging times, the microstructure near the center of the disc consists of large semi-coherent LiFeO_2 particles in $\text{LiFe}_{5/8}\text{O}_8$. These have characteristics similar to the ones discussed earlier for Stage I particles. In regions near the surface of the heated crystal one sees a single phase microstructure. The single phase is a spinel phase as confirmed by the selected area electron diffraction pattern. The thin foils show a high density of small angle tilt boundaries with numerous dislocations in between. Figure 7a shows one such boundary and Fig. 7b is the SAD pattern obtained with the selected area aperture place over the boundary to include portions of both the grains. From this pattern, the misorientation is found to be about three degrees about the $[1\bar{1}0]$ direction between the two grains. The dislocations have a Burgers vector of $1/2\langle 110 \rangle$.

(iii) The Final Stage (Stage III): As shown schematically in Fig. 1, in stage III, the entire crystal has a polygranular single phase microstructure. The details are similar to the features of the near-surface regions of Stage II, which were discussed above.

On reaging such a sample at 750°C (where lithium ferrite shows an order-disorder transition), all the superlattice reflections⁽¹⁷⁾ of ordered lithium ferrite are visible from all grains. Since the ordering is due to rearrangement of lithium atoms in the octahedral

interstices, this proves the presence of Li throughout the material.

On further aging (>3 hrs), a microstructure with opaque particles (~1000 Å in diameter) dispersed in spinel as in Fig. 8a is obtained near the center of the sample. The particle contrast is always dark in bright fields as well as in dark fields, and the contrast does not change with $\vec{g}$, sign of s , or thickness of the foil. This suggests that the particles are amorphous. Although one would expect to see diffuse rings from amorphous particles, the low volume fraction ($\leq 1\%$) of this phase does not contribute enough intensity to the electron diffraction pattern. No glassy particles are present near the crystal surface.

(b) Transformation in Vacuum

As noted earlier, the features of the phase transformation in vacuum are similar to those in air, with the exception of the reaction kinetics. In fact, the initial transformation stage is not observed in the thin platelet samples even for the shortest annealing times. Stages II and III are similar to those in air. The additional observation in the vacuum annealed specimens is the formation of amorphous particles for shorter aging times. In Stage II, the amorphous particle density increases very rapidly and reaches a maximum. For very long aging times the amount of amorphous particles decreases. The amorphous particles have a nearly spherical shape, although in a few cases these are elongated. There is no detectable strain in the matrix around these particles. Figure 8b shows the preferential growth of the amorphous particles at the LiFe_5O_8 - LiFeO_2 interface in Stage II of the transformation. As can be seen in Fig. 8b, no amorphous inclusions are present in the LiFeO_2 phase.

(c) Transformation in Oxygen

Here again, the morphology of the transformation is the same as that in air except for the kinetics, but unlike the vacuum-annealed case, the reaction is very slow. The two phase microstructure corresponding to Stage II is shown in Fig. 9 where part of an elongated semicoherent precipitate is imaged. The misfit as measured here corresponds to the value of δ obtained earlier. The amorphous phase forms only for very long annealing times. Roughly 10-12% of LiFe_5O_8 transforms to LiFeO_2 .

(d) Transformation in Polycrystalline Material

The sintered polycrystalline material is single phase spinel with the largest grain size of about 5μ . This was annealed in vacuum for times corresponding to Stage II and Stage III of the transformation. Of special significance is the observation that, even after heating for very long times, no amorphous phase appears unlike the vacuum-annealed single crystals. Figure 10 taken from foils near the center of the crystal, shows LiFeO_2 particles form in the grain interior as well as on the grain boundary. The role of the grain boundaries in the transformation kinetics has not been systematically investigated in this study.

IV. DISCUSSION

(a) Formation and Growth of LiFeO_2 Particles

LiFeO_2 has the rock salt structure with oxygen at the anion sites and a random distribution of Li and Fe at the cation sites⁽¹⁸⁾. The distribution of anions on closepacked $\{111\}$ planes in LiFeO_2 and LiFe_5O_8 are almost identical (separation between oxygen ions are 2.927 Å and 2.945 Å respectively). The cations in LiFe_5O_8 are arranged

in alternate Kagomé and mixed layers⁽¹⁹⁾ where as cations in LiFeO_2 are arranged in close packed layers. From the ASTM data file, the misfit between the two lattices is only 0.6% and thus the strain energy due to the precipitates is quite small. The formation of octahedral shaped precipitates with {111} planes as faces suggests that the shape is determined by the anisotropy of the interfacial energy. Undoubtedly {111} interfaces in this case have the lowest surface-free energy. For a given volume, tetrahedral precipitates have nearly 20% more area than octahedral precipitates and thus, for negligible strain energy, octahedral particles are preferred. It may be noted that larger strains may change the morphology⁽²⁰⁾ of the particles as seen in the case of wüstite precipitates in CoFe_2O_4 ⁽²¹⁾. Since the anion positions remain unchanged in the precipitation process, and since cations are very mobile in the spinel structure⁽²²⁾, the formation and growth of LiFeO_2 particles can be viewed simply as a process of diffusion and redistribution of cations. The phase transformation is discussed further in section IV(b).

As in Fig. 10, LiFeO_2 Particles also form inside the grains in a polygranular LiFe_5O_8 sample. Because of the high diffusivity of the cations in the spinel structure, it may be possible to suppress heterogenous precipitation on grain boundaries to obtain a homogeneous dispersion of precipitates, if desired.

(b) Nature of the Phase Transformations during Material Loss

The results described earlier can be interpreted by considering the reaction postulated by Salmon and Marcus⁽¹¹⁾:

LiFeO_2 would then be an intermediate product in the decomposition. If reactions (1) and (2) occur at an equal rate i.e. if LiFeO_2 decomposes at the same rate as it is being formed, then one should find it only at the surface of the sample. It is clear from the above observations that this is not the case. It is possible to explain the present results if one assumes that reaction (1) proceeds faster than reaction (2); or, in more general terms, if oxygen is lost at a higher rate than lithia. As a result an excess of cations or alternatively an oxygen deficit is created within the spinel phase, causing the precipitation of the cation rich LiFeO_2 phase. The precipitation process starts at first at the surface. As the oxygen loss at the surface continues, the oxygen deficiency is gradually transmitted to the interior of the sample through diffusional processes, the nature of which are not known, but need not be specified here. As a result, precipitation occurs throughout the sample (Stage I). However, near the surface, the oxygen deficiency is more severe, and hence at this stage there is more LiFeO_2 present near the surface than in the interior. On the other hand, the loss of lithia is also gradually felt. This causes the dissolution of the lithia rich LiFeO_2 phase, again starting first near the surface. In stage II (Fig. 1) the outer surface layers lose enough lithia so that the LiFeO_2 dissolves again leaving behind the interface dislocations introduced during the precipitation process. Ultimately, in samples which are thin enough, reaction (2) catches up with reaction (1) even at the center of the sample and only the spinel phase remains with the remnants of the interface dislocations and boundaries (stage III). This spinel phase still contains some lithium depending on the atmosphere. This point has been investigated by Tretyakov et al⁽¹³⁾. In the present case, when annealed in air, enough lithium is still present to observe the

order-disorder reaction as described earlier. This is also apparent from the chemical analysis results given in Table III. It is clear that in thick crystals, stage III, may never be reached and that a two phase state is obtained in the interior of the sample. An example is shown in Fig. 11 taken from the center of a crystal, 2 cm in diameter annealed in vacuum for 10 hours. The interior of the crystal contains LiFeO_2 precipitates several microns in diameter. It is important to realize this when processing lithium-ferrite. In polycrystalline material, the lithium ferrate can form as precipitates within the spinel grains (Fig. 10).

In summary, the phase transformations observed during the material loss of lithium ferrite are due to the competition between the oxygen loss and the lithia loss. These phase transformations can be understood by plotting the local composition at a constant depth in the sample as a function of time in the Fe_3O_4 - Fe_3O - Li_2O phase diagram as determined by Tretyakov et al. (Fig. 12). Schematically the path ABC will be followed, where branch AB is due to the oxygen loss at constant lithia content, and branch BC is due to the lithia loss at constant Fe^{2+} content. Regarding the reactions by Salmon and Marcus, the remark needs to be made that the LiFeO_2 is not strictly an intermediate product in the sense that it is a necessary step in the lithia loss process, as this phase is not found near the surface of the samples in stage II. Lithia loss can take place independently from the oxygen gas loss through the reaction:

The $\gamma\text{-Fe}_2\text{O}_3$ forms a solid solution with the lithium ferrite. Nevertheless, reactions (1) and (2) can still provide a useful framework for the discussion of the material loss processes.

(c) The Amorphous Particles:

The absence of any amorphous particles in sintered polycrystals in spite of their presence in the flux-grown single crystals rules out the possibility that this phase is characteristics of the Li-Fe-O system. The chemical analysis of single crystal $\text{LiFe}_{5/8}\text{O}_8$ as given in Table I shows the presence of some glass forming impurities retained from the flux and most probably the amorphous phase is a low melting complex oxide of some of these impurities. The gradient in their distribution with the depth of the foil indicates that the phase is very volatile. No attempt has been made in this investigation to characterize the amorphous phase further.

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TABLE I.

Semiquantitative spectrographic analyses of as grown LiFe_5O_8 single crystal.

Constituent Element	Amount (wt. % as oxides)
Fe	Principal Constituent
Pb	15.0
B	4.0
Li	2.0
Pt	0.15 (as metal)
Mn	0.025
Al	0.01
Si, Mg, Ca, Ni, Cr, Mo	< 0.005

TABLE II.

Annealing times for 15 mil thick discs

	Air	Vacuum (10^{-5} torr pressure)	Oxygen (760 torr pressure)
Stage I	15-30 minutes	-----	30-45 minutes
Stage II	30-60 minutes	≤ 60 minutes	45-75 minutes
Stage III	>60 minutes	≥ 60 minutes	>75 minutes

TABLE III.

Lithium and iron contents as determined by a semiquantitative chemical analysis.

Atmosphere	Annealing times	<u>Li</u> (wt%)	<u>Fe</u> (wt%)
-----	As received	1.62	63.84
Air	Stage I	1.54	67.44
	Stage III	1.17	68.57
Vacuum	Stage II	1.51	67.73

Figure Captions

- Figure 1. Sketch to show the position of the LiFeO_2 phase and the small angle boundaries inside the LiFe_5O_8 crystal as the phase transformation proceeds. The three stages are distinguished by the microstructure-depth relationships as shown. Amorphous particles are not shown.
- Figure 2. Bright field image showing octahedral precipitates of LiFeO_2 in LiFe_5O_8 matrix. This BF micrograph, near $[110]$, shows the projection of the octahedra with depth oscillation fringes due to inclined $\{111\}$ faces. The particles have negligible strain contrast around them.
- Figure 3. (a-c) Selected area diffraction patterns from LiFe_5O_8 , $\text{LiFeO}_2 + \text{LiFe}_5\text{O}_8$ and LiFeO_2 regions respectively. Note the diffuse scattering in (b) and (c) arising due to short range order in LiFeO_2 . The indices marked in the reciprocal lattice section in (d) correspond to those of the spots adjacent to the transmitted beam in the direction of the arrows.
- Figure 4. BF and DF images of LiFeO_2 in LiFe_5O_8 . DF_1 and DF_2 are taken using spots 1 and 2 marked in the diffraction pattern in the inset (BF image). Note the presence of diffuse scattering from LiFeO_2 in the diffraction pattern.
- Figure 5. BF Micrographs showing (a) isolated LiFeO_2 precipitates as they lose coherency with the matrix, (b) precipitates growing

preferentially on dislocations, (c) part of a long LiFeO_2 precipitate (B) due to the anisotropic nature of the growth. The morphology in (C) is due to impingement of a row of growing precipitates.

Figure 6. (a) and (b) are images of precipitate-matrix interface dislocations $\{\text{LiFeO}_2 - \text{LiFe}_5\text{O}_8\}$ imaged in different diffracting conditions so as to show one set of the interfacial dislocations in contrast at one time. The figures show only part of a long LiFeO_2 precipitate in a thick foil.

Figure 7. (a) BF image of a small angle boundary in the transformed LiFe_5O_8 with the second order reflection excited. Foil normal near $[110]$ pole. (b) Symmetrical $[110]$ electron diffraction pattern with the selected area aperture covering portions of the grains on either side of the boundary in (a).

Figure 8. (a) BF image of uniformly dispersed amorphous particles in LiFe_5O_8 matrix after annealing in air. (b) Amorphous particles growing preferentially at the semicoherent $\text{LiFeO}_2 - \text{LiFe}_5\text{O}_8$ interface in vacuum annealed LiFe_5O_8 .

Figure 9. BF image showing portion of a long LiFeO_2 precipitate in LiFe_5O_8 annealed in one atmosphere of oxygen at 1200°C . The second order reflection for the matrix (or the first order spot for the precipitate) is used to image the interface dislocations, which are dissociated as

$$1/2\langle 110 \rangle = 1/4\langle 110 \rangle + 1/4\langle 110 \rangle$$

Figure 10. Semicoherent LiFeO_2 precipitates (a) on a grain boundary and (b) in the grain interior in LiFe_5O_8 polycrystals. Note the precipitates A and B in (a) growing into grain 2 but retaining a flat interface with respect to grain 1.

Figure 11. BF image showing the duplex microstructure in a large LiFe_5O_8 crystal. I is part of a semicoherent LiFeO_2 precipitate in the matrix II, and is imaged with the matrix 004 reflection excited.

Figure 12. Sketch of the isothermal ternary section of the $\text{FeO}-\text{Fe}_2\text{O}_3 - \text{LiFeO}_2$ phase diagrams from ref. 12. $A \rightarrow B \rightarrow C$ is the schematic direction of the transformation path.

XBL 765-6875

FIG. 1

XBB 766-5390

FIG. 2

XBB 766-5398

FIG. 3

FIG. 4

XBB 760-10297

XBB 766-5352

FIG. 5

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FIG. 6

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FIG. 7

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FIG. 8

XBB 766-5357

FIG. 9

XBB 7610-9577

FIG. 10

FIG. 11

XBB 766-5356

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XBL 765-1986

FIG. 12

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720