

The Production of Lithium Oxide by Electron Irradiation of Lithium Fluoride

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Observations of electron damage occurring in LiF single crystals within an electron microscope are recorded. A number of irradiation-induced defects, similar to those reported by other workers were observed, but a new feature is the identification, by electron diffraction, of Li₂O distributed in precipitates and as a dispersed phase.

1. Introduction

The precipitation of Li in neutron-irradiated LiF has been investigated by many radiation damage workers using a variety of techniques. X-ray diffraction studies [1-3] have shown that after exposure to neutron doses exceeding about 10^{17} nvt, platelets of metallic Li are formed on the {100} planes of the LiF parent lattice. Lambert *et al* [4] have confirmed the identification of these platelets as Li by differential thermal micro-analysis and these workers have further demonstrated that the Li exhibits an anomalous fcc structure. The presence of metallic Li in such material has also been established by nuclear magnetic resonance [5-7] and electron spin resonance [7] measurements.

Carroll and Birnbaum [8] produced plate-like precipitates by irradiating LiF with ions that were formed by introducing oxygen through a controlled leak near the filament of an electron microscope. From electron diffraction observations they identified them with the anomalous fcc structure reported by Lambert *et al* [4].

Electron irradiation damage occurring in LiF has been recorded by Tanaka *et al* [9] who observed voids to grow from about 200 to about 1000 Å in diameter during transmission electron microscopy. Using much lower beam current densities to reduce specimen heating, Mannami *et al* [10] reported the formation of point defect clusters of 30 Å in diameter. These subsequently grew under continued electron irradiation to the size of the voids seen by the workers mentioned in the previous reference. However, the production of Li precipitates is not recorded in either of these reports.

In the present study a precipitation process arising from electron irradiation was observed but the precipitates in this case have been identified by electron diffraction as Li₂O. Two types of damage were produced; one being termed ordered and the other disordered. In the former the Li₂O took the form of plate-like precipitates lying in {100} planes of the LiF lattice, while in the latter it was randomly distributed together with polycrystalline LiF. Identification of Li₂O is supported by an independent experiment in which Li metal was evaporated on to an amorphous carbon substrate which was subsequently examined by electron diffraction.

2. Experimental

2.1. Specimen Preparation

LiF specimens were prepared from good quality material supplied by Dr D. A. Jones of the Department of Natural Philosophy, University of Aberdeen. Cleaved flakes of about 0.02 cm in thickness were chemically thinned and polished using 40% fluoroboric acid. The specimens were then clamped between two 200-mesh copper grids for observation in a Philips EM300 electron microscope.

Li metal of 99% purity, obtained from British Drug Houses Ltd, was evaporated to give a film thickness of the order of 200 Å on an amorphous carbon substrate of similar thickness which was mounted on an electron microscope grid. The evaporation was carried out at a pressure of less than 10^{-4} torr. On removal from the coating unit the films were transferred to the electron microscope where they were investigated by diffraction.

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2.2. Specimen Examination

The accelerating voltage at which the electron microscope was operated throughout this work was 100 kV.

In addition to the use of an anti-contamination device, the following two independent techniques were employed to eliminate bombardment of the specimen with ions.

(a) A carbon film of the order of 200 Å in thickness was placed across the aperture of the first condenser lens [11].

(b) A transverse magnetic field was applied to the beam directly below the illumination system

using the beam centralising device of the electron microscope. The electron spot was brought back to the electron-optical axis of the microscope by mechanically misaligning the whole of the double condenser lens arrangement.

3. Results and Discussion

3.1. Ordered Damage

By employing low beam currents LiF could be observed by transmission at a screen magnification of a few tens of thousand times without noticeable electron damage. However, on increasing the beam current density to maintain an

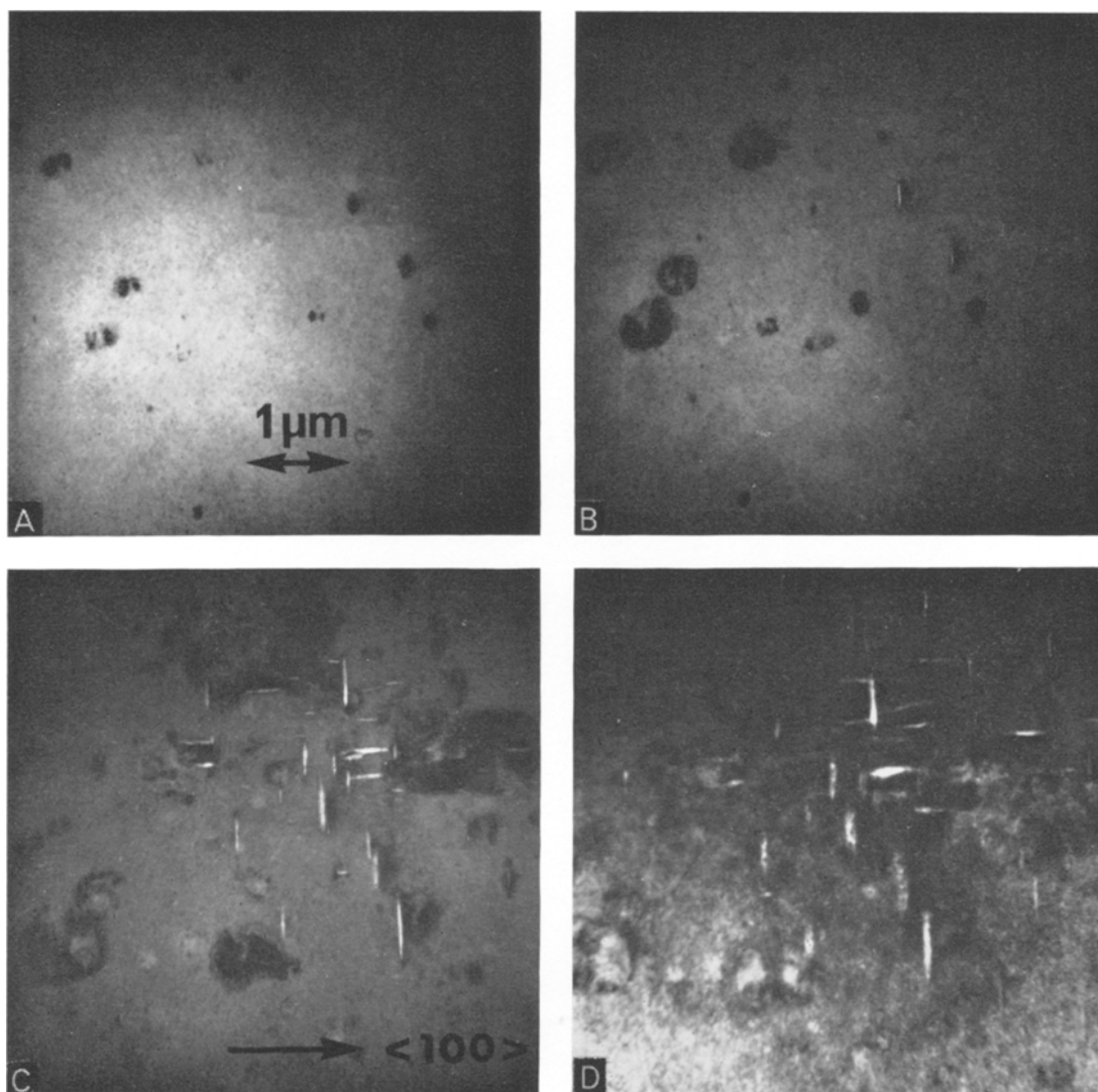


Figure 1 Sequence showing development of voids and Li_2O precipitates produced by electron irradiation of LiF.

adequate level of intensity for visual observation at higher magnifications, damage processes were induced as shown in the time sequence of fig. 1. These micrographs were recorded at 20 sec intervals using a beam current of $10 \mu\text{A}$ with the exception of fig. 1d which was taken after an additional exposure of 20 sec with the beam current increased to $40 \mu\text{A}$. This latter adjustment was made because no significant changes were observed after 20 sec of irradiation at $10 \mu\text{A}$ following the recording of fig. 1c. After a further increase in beam current no new features were produced beyond the state shown in fig. 1d. The important aspects of this damage sequence are:

(a) The double loop structures of diffraction contrast.

(b) The regions of light contrast which lie in the (100) and the (010) planes of the LiF lattice.

The loops have been identified by dark-field illumination with the voids produced by electron irradiation of LiF as discussed by Tanaka *et al* [9]. From fig. 1 the extent of their associated strain fields can be seen to increase from a diameter of about $0.1 \mu\text{m}$ to a maximum of about $1 \mu\text{m}$. This is an order of magnitude larger than that observed by the above workers and it is proposed that this, together with the production of precipitates, might be attributed to a larger beam current density resulting in a higher specimen temperature than that in the experiments of Tanaka *et al*.

The regions of light contrast closely resemble

the precipitates that were produced during oxygen ion irradiation of LiF by Carroll and Birnbaum [8]. They are of comparable size (of the order of $1 \mu\text{m}$ in length and a few hundred \AA in thickness) and in fig. 1d after the increase in beam current density, they similarly appear to become more diffuse at higher specimen temperatures. However, further investigations have eliminated the possibility of their identification with the anomalous fcc structure suggested by the work of the above authors.

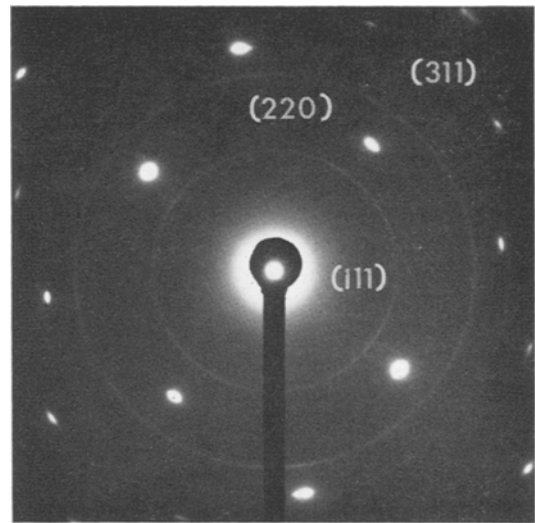


Figure 2 Selected area diffraction pattern from region containing ring ordered damage similar to that in fig. 1c.

TABLE I Analysis of diffraction pattern in figure 3

Nature of pattern	Diameter in cm	Measured D-spacing		Identification	
		\AA	\AA	LiF	Li_2O
ring	3.9	2.64	2.66		(111)
spot	4.45	2.31	2.32	(111)	
diffraction ring apparently absent			2.31		(200)
spot/ring	5.1	2.015	2.01	(200)	
ring	6.35	1.62	1.63		(220)
spot	7.25	1.42	1.42	(220)	
ring	7.4	1.38	1.39		(311)
diffraction ring apparently absent			1.33		(222)
spot	8.5	1.21	1.21	(311)	
ring	8.9	1.155	1.15		(400)
ring	9.7	1.06	1.06		(331)
diffraction ring apparently absent			1.03		(420)
spot	10.2	1.01	1.005	(400)	
ring	10.95	0.940	0.941		(422)
spot	11.15	0.923	0.922	(331)	
spot	11.45	0.900	0.898	(420)	
spot	13.25	0.777	0.773	(511)	
spot	14.5	0.710	0.711	(440)	
spot	15.05	0.685	0.679	(531)	
spot	15.35	0.670	0.670	(600)	
spot	16.20	0.635	0.635	(620)	
spot	17.00	0.605	0.606	(622)	

The selected area diffraction pattern taken from a damaged region containing a high proportion of voids was not noticeably different from that taken from an undamaged region. However, when precipitates were formed diffraction rings appeared and increased in intensity as shown in fig. 2 which corresponds to a region like that seen in fig. 1c. The three diffraction rings index as the (111), (220) and (311) reflections of a cubic system with a lattice parameter of $4.60 \pm 0.05 \text{ \AA}$. For reasons that are discussed later these results have been used to identify the precipitated phase as Li_2O . The identification of the precipitates with the polycrystalline diffraction pattern was confirmed by dark-field observation using electrons selected from part of the (111) diffraction ring.

3.2. Disordered Damage

While the damage just described could be arrested at any stage in its development this did not apply when high current densities were used for short periods of time. In the extreme case the sudden application of an intense beam resulted in crystals exploding and small crystallites being ejected. At somewhat lower current densities however, the damage was less catastrophic and its characteristics are revealed by the interpretation of fig. 3, which is a selected area diffraction

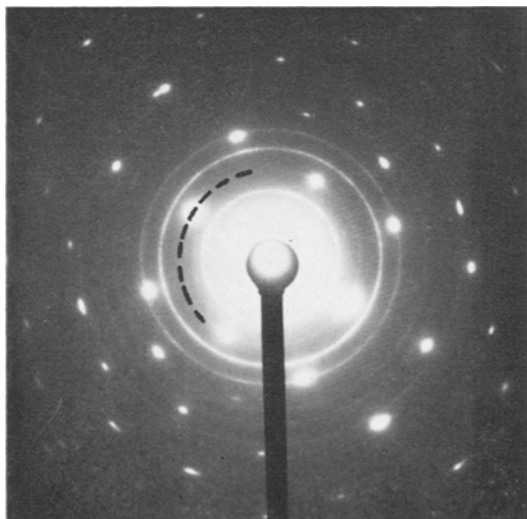


Figure 3 Selected area diffraction from a disordered damage region. The pattern of spots is due to diffraction from single crystal LiF. The ring pattern is derived from polycrystalline Li_2O with the exception of the dotted ring which illustrates diffraction from polycrystalline LiF.

pattern taken from such a damaged region. From table I this pattern can be seen to comprise:

(a) Spots from the LiF lattice corresponding to a (100), a (310) and a (510) zone axis, suggesting severe buckling over a small region of the specimen.

(b) A low intensity polycrystalline ring coinciding with the (200) spot of the LiF lattice and some faint arcs passing through other LiF reflections. These observations demonstrate that polycrystallisation of the single crystal material is produced by electron irradiation. It is suggested that this process might account for the apparent dispersion of the precipitates observed in ordered damage at large beam current densities.

(c) A set of polycrystalline rings, the first three of which can be identified with those arising from the precipitates of ordered damage. The additional rings in this pattern make it possible to identify this phase unambiguously as follows. The (200), (222) and (420) reflections are apparently absent from an otherwise fcc structure with a lattice parameter of $4.60 \pm 0.05 \text{ \AA}$. These absences discount the identification of this phase as an anomalous fcc form of lithium and identify it as Li_2O which has the calcium fluoride structure and a lattice parameter of 4.612 \AA [12]. A simple calculation shows that there was sufficient residual oxygen in the specimen chamber of the electron microscope to account for the degree of oxidation observed.

Theoretical estimates of the structure factors [13] for the first eight reflections of Li_2O are given in table II. In this table the apparent absences of

TABLE II Calculated structure factors for Li_2O

Reflection	$\frac{\sin\theta}{\lambda} (\text{\AA}^{-1})$	Structure factor F	F*	F ²
(111)	0.188	f_{0-}	5.8	33.6
(200)	0.217	$f_{0-} - 2f_{\text{Li}+}$	1.6	2.56
(220)	0.307	$f_{0-} + 2f_{\text{Li}+}$	6.7	44.9
(311)	0.360	f_{0-}	3.1	9.61
(222)	0.376	$f_{0-} - 2f_{\text{Li}+}$	0.2	0.04
(400)	0.436	$f_{0-} + 2f_{\text{Li}+}$	4.9	24.0
(331)	0.475	f_{0-}	2.2	4.84
(420)	0.486	$f_{0-} - 2f_{\text{Li}+}$	0.05	0.0025

the (222) and (420) diffraction rings are clearly accounted for but that of the (200) is not satisfactorily explained. It is suggested that this might be attributed to the fact that atomic scattering factors are less reliable [14] at small values of $\sin \theta/\lambda$.

3.3. Evaporated Lithium Experiment

Electron diffraction observations showed that even when care was taken to maintain a pressure of less than 10^{-4} torr while evaporating Li, the films produced always comprised at least two phases, these being Li and Li_2O . In most cases many extra diffraction rings were observed and measurements suggested that these could be attributed to Li_2CO_3 and LiOH . However, after exposure to a moderate beam current density for a few seconds the intensity of these and also the Li reflections became weaker while that of the Li_2O rings increased. A diffraction pattern recorded at this stage is shown in fig. 4 and its

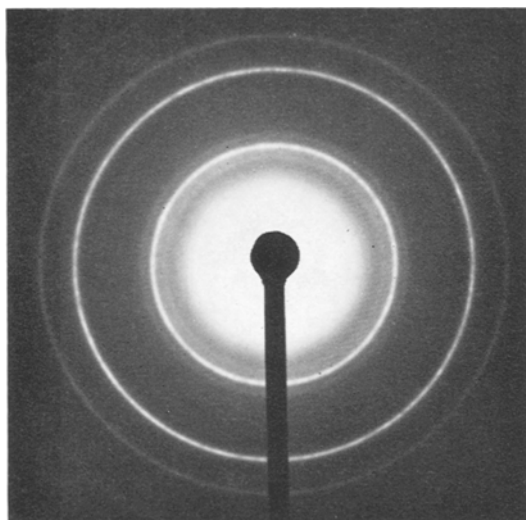


Figure 4 Diffraction pattern from a film obtained by evaporating lithium metal showing rings due to Li_2O and Li_2CO_3 . The three most intense rings (from Li_2O) may be compared with those in fig. 2.

indexing data are presented in table III. Apart from a difference in scale introduced during photographic enlargement, this independently obtained electron diffraction pattern from polycrystalline Li_2O is identical to that seen in fig. 3. As in the experiments on disordered damage no evidence was found of the weak (200) reflection suggested by the theoretical estimate of structure factors for Li_2O given in table II. The observed decrease in relative intensity of the Li diffraction rings provides additional evidence of the oxidation of this metal produced by electron irradiation within the electron microscope.

TABLE III Analysis of diffraction pattern in fig. 4

Ring diameter in cm	Measured	Calculated	Identification	
	D-spacing Å	D-spacing Å	Li_2O	Li_2CO_3
5.9	4.13	4.18		(110)
8.2	2.97	2.93		(20 $\bar{2}$)
8.7	2.82	2.83		(002)
9.2	2.65	{ 2.64	(111)	
10.0	2.45	{ 2.64		(11 $\bar{2}$)
		2.44		(31 $\bar{1}$)
diffraction ring				
apparently absent		2.29	(200)	
13.25	1.85	1.87		(311)(022)
15.1	1.61	1.62	(220)	
17.75	1.37	1.38	(311)	
diffraction ring				
apparently absent		1.32	(222)	
21.3	1.145	1.14	(400)	
23.3	1.045	1.05	(331)	
diffraction ring				
apparently absent		1.02	(420)	
26.2	0.93	0.935	(422)	

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