JOURNAL OF MATERIALS SCIENCE 21 (1986) 4385–4390

Microhardness response of nitrogen-implanted and X-irradiated lithium fluoride

S. G. ROBERTS*, T. F. PAGE
Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge, UK

The microhardness behaviour of {0 0 1} faces of LiF has been investigated before and after both nitrogen-ion implantation and implantation followed by X-irradiation. Implantation alone produced no changes in either hardness or dislocation etch-pit rosette sizes on the surface, though radial indentation fracture was promoted. Implantation followed by X-irradiation produced high densities of colour centres deep into the crystal, much deeper than the implantation damage depth ($\sim 0.2\,\mu m$). Hardness and rosette sizes were affected to depths of $\sim 150\,\mu m$, which was less than the colouration depth. Thus the "colour centres" producing the colour are probably different from those impeding dislocation motion.

1. Introduction

The investigations reported here formed part of a broader study aimed at investigating the basis of the observations of Dearnaley [1] that nitrogen implantation to doses greater than $4 \times 10^{17}\,cm^{-2}$ could significantly improve the wear lifetimes of WC–Co cemented carbides. Since, at the time the work was performed, there had been otherwise very few investigations of the effects of ion implantation on the mechanical properties of non-metals, especially ceramics, the study [2] investigated the effects of implantation (mainly of N_2^+) on several materials covering a wide range of bond types and plastic/brittle character (e.g. silicon, silicon carbide, alumina, WC–Co, cobalt, LiF, inorganic and metallic glasses). Results from the studies on silicon and silicon carbide have already been reported [3, 4], where it was established that high-dose N_2^+-implantations ($> \sim 4 \times 10^{17}\,cm^{-2}$) into both materials produced a marked surface softening (as measured by low-load indentation tests at room temperature), together with suppression of the lateral type of indentation fracture. Later studies made more detailed investigations of the structural changes leading to surface softening in these and other ceramic materials [5–8], and also the generation of implantation-induced surface stresses and their effects on indentation fracture behaviour [9].

The present paper deals with the effects of nitrogen implantation on the microhardness and indentation fracture behaviour of a predominantly ionic solid, LiF. The effects of implantation (to produce displacement damage) followed by X-irradiation (to produce colour centres from this damage) were also studied. Study of the variation of the measured hardness with indentation size, and of the variation of etch-pit rosette size both with dose and with depth into the crystal, has allowed some conclusions to be drawn about the mechanical properties of the thin ($< 0.5\,\mu m$) near-surface implanted layer. Indentation fracture patterns and the detailed structure of the rosettes around indentations were examined by light microscopy and by scanning electron microscopy (SEM). It was found that implantation alone had no measurable effect on the microhardness behaviour of LiF, but that implanted samples showed {1 0 0} and {1 1 0} radial cracks around indentations on {0 0 1} planes at loads ($< 500\,g$) where unimplanted material showed no cracking at all.

Plastic flow in LiF is known to be affected by the charge resulting from ionizing radiation, which produces "colour centres". These are localized electrically charged defects of various configurations (e.g. [10]). Dislocations in ionic materials have electrically complicated core structures. In particular, kinks and jogs have an associated charge. Dislocations can therefore be strongly pinned by charged defects, and so lithium fluoride can be hardened by X-irradiation [11, 12] and also by impurity atoms of different valency (e.g. [13]).

In contrast to X-irradiation, ion implantation would be expected to produce damage by displacements rather than by ionization (e.g. [14]). The damaged layer would also be very thin (less than $0.5\,\mu m$) compared with the penetration distance of X-rays (the intensity in LiF for Cr$K\alpha$ decays exponentially over a depth of $\sim 0.3\,mm$ [15]). In this study, the effects of implantation alone and of implantation followed by X-irradiation were examined by microhardness testing and dislocation etch-pitting.

2. Experimental details

2.1. Lithium fluoride

Lithium fluoride (LiF) is an ionic solid with the sodium chloride crystal structure. Crystals cleave readily on {1 0 0} and less easily on {1 1 0}; large single crystals of known orientation can be easily prepared.

*Present address: Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford, UK.

0022–2461/86 $03.00 + .12

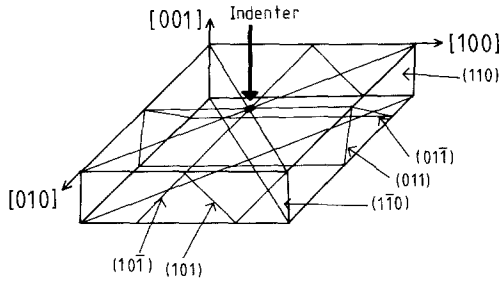

Figure 1 The arrangement of slip planes around a Vickers indenter on an {0 0 1} plane in LiF. The inclined planes are termed $\{1\,1\,0\}_{45}$ planes; the planes normal to the surface are termed $\{1\,1\,0\}_{90}$.

Following the initial study of Gilman and Johnston [16], who showed how etching could reveal the surface positions of dislocations, the relationships between dislocation behaviour and macroscopical mechanical properties of LiF have been extensively researched. The principal slip systems at room temperature are of the type $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$. Microhardness indentations produce large dislocation loops on {1 1 0} planes, which can be revealed by suitable etching as "rosettes" around the indentations (e.g. [17]). The slip plane geometry around an indentation on an {0 0 1} plane is shown in Fig. 1, and a typical rosette is shown in Fig. 2a. Rosette diameters for indentations in the load range used here (5 to 200 g) ranged from 20 to 200 μm (see Section 3).

2.2. Preparation and etching

Specimens were prepared by cleavage from larger crystals, supplied by Messrs Specac Ltd (Orpington, UK). The implanted specimens were cleaved immediately before implantation in the "Pimento" machine at UKAEA Harwell (see below), and subsequently kept in a well-sealed box containing absorbent silica gel. This was in an attempt to avoid the contamination of the active surfaces with water, which degrades the surface finish and can alter the hardness behaviour [18]. Etching was performed in saturated FeF_3 solution at 70° C [16]. Production of good etch pit rosettes took 2 to 10 min (the implanted specimens in particular were found to need long etching times). The specimens were examined by light microscopy and by SEM. For the latter, a thin sputtered coat of gold was applied, which was also found to improve contrast for light microscopy.

2.3. Implantation

Specimens were implanted with nitrogen ions at UKAEA Harwell, using the "Pimento" prototype commercial implanter, operating at 80 kV. The beam was estimated to consist of ~ 80% N_2^+ ions (which are assumed to dissociate to pairs of 40 kV particles at the specimen surface [19]). Thus the total dose of nitrogen is 1.8 times the stated dose of N_2^+. The average dose rate was 5.8 μA cm^{-2} (3×10^{12} ions cm^{-2} sec^{-1}), giving an estimated specimen temperature during implantation of 300° C. The specimens were rotated in the ion beam to ensure uniformity of dose. Specimens were oriented with an {0 0 1} face normal to the centre line of the ion beam; thus some at least of the incident ions would be travelling in a $\langle 1\,0\,0\rangle$ direction and might therefore be channelled. A series of specimens was prepared, the lowest dose being 10^{17} cm^{-2} and the highest 6×10^{17} cm^{-2}.

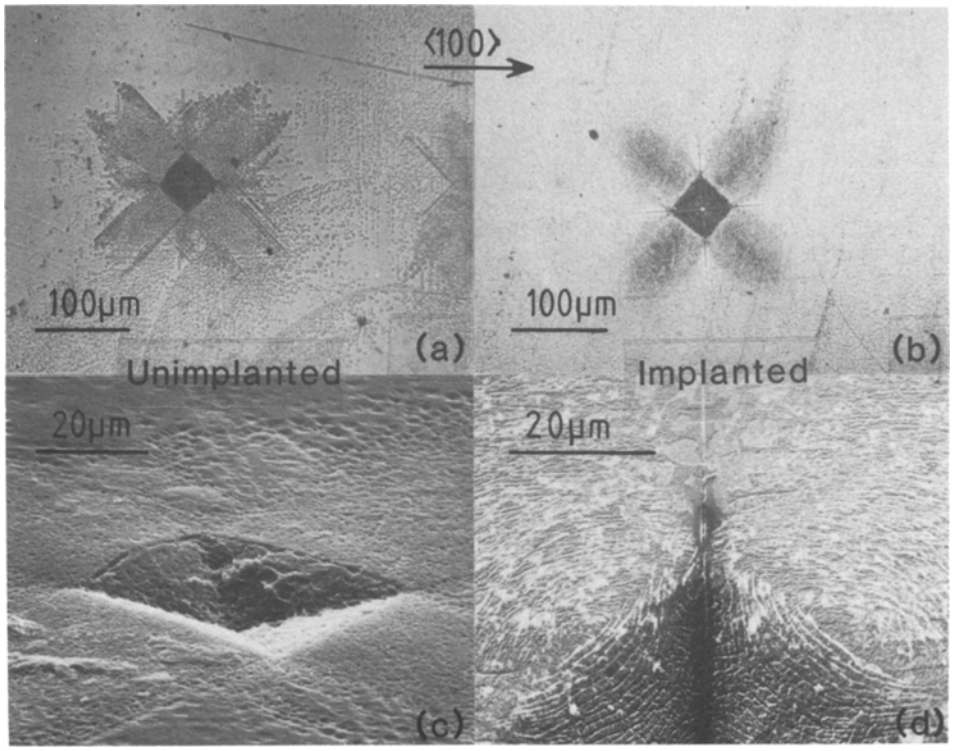

Figure 2 Rosettes around 200 g indentations in unimplanted (a, c) and implanted (b, d) (dose 6×10^{17} cm^{-2}) LiF. (a, b) are reflected micrographs, (c, d) SEM (secondary electron) images. Note the radial cracks in implanted LiF ($\langle 1\,0\,0\rangle$ traces), and the different etching behaviour of the $\{1\,1\,0\}_{90}$ rosette arms before and after implantation. However, the extents of the rosette arms are similar.

TABLE I Indentation size effect and hardness of implanted and unimplanted LiF

Dose	ISE index (n)*	$H_{10\,\mu m}$ (GPa)	H_{200g} (GPa)
zero	1.99 ± 0.05	1.10 ± 0.08	1.10 ± 0.04
$6 \times 10^{17}\,cm^{-2}$	1.99 ± 0.06	1.08 ± 0.09	1.05 ± 0.03

*Hardness (H) variation with indentation diagonal (d) is fitted to the equation $H = d^n$.

3. Microhardness testing of unirradiated LiF

3.1. Hardness results

Tests were performed on freshly cleaved unimplanted LiF and on specimens implanted to a dose of $6 \times 10^{17}\,cm^{-2}$. A standard Leitz "Miniload" microhardness tester was used, fitted with a Vickers profile indenter. The diagonals of all indentations were aligned along <1 0 0> directions on the specimens, so as to minimize the effects of hardness anisotropy [20]. All indentations were made at room temperature in ambient laboratory conditions. The load range used was 5 to 200 g, with a dwell time of 20 sec, yielding indentations with diagonals of ~ 10 to 60 μm, and depths of ~ 1.5 to 8 μm.

For 80 keV N^+ ions into LiF, the peak of the Gaussian ion range profile (R_p) is ~ 0.18 μm beneath the surface, with a range straggling (ΔR_p) of ~ 0.4 μm. The corresponding figures for the damage profile are: peak (X_D) ~ 0.14 μm, straggling (ΔX_D) ~ 0.03 μm. For 40 keV N^+ ions, the corresponding figures are: $R_p = \sim 0.09\,\mu m$, $\Delta R_p = \sim 0.03\,\mu m$, $X_D = \sim 0.07\,\mu m$, $\Delta X_D = \sim 0.02\,\mu m$. These figures were calculated [21] using a simplified form of the computer code given by Manning and Mueller [22], and show that, at low indentation loads, a significant proportion of the indentation depth lies within the implantation-affected layer.

Hardness data were analysed by the method of Sargent [18] (as detailed in [4, 23]); a computer program gives an indentation size effect (ISE) index and an interpolated hardness at a standard indentation diagonal (10 μm in this case). Results are shown in Table I. It can be seen that both implanted and unimplanted LiF have an ISE index of ~ 2 (i.e. hardness is independent of indentation size in this load range). This is in contrast with most ceramic materials (e.g. [4]), in which the ISE index is less than 2 (i.e. hardness increases with decreasing indentation size). Thus for LiF implanted with N_2^+, no softened or hardened surface layer is detectable by low-load hardness testing.

3.2. Rosettes

Indentations in LiF are surrounded by a highly structured region of plastic flow consisting of large dislocation loops on {1 1 0} planes (see Fig. 1). The sizes of these "rosettes" have been found to be highly sensitive to the ease of plastic flow, more so, indeed, than the hardness value itself (e.g. [17]). The large depth of the "plastic zone", compared to that of any implantation-affected surface-layer, probably accounts for the null result of implantation on hardness values. Even if the layer is harder or softer than the parent material, subsurface plastic flow probably controls the hardness (e.g. [24]). However, it was thought that measurement of rosette size might give an indication of any change in dislocation mobility in the surface layer (as has subsequently been shown for MgO by Burnett and Page [7, 24], where a hardened surface layer was shown to be produced by implantation of Cr^+, Ti^+ and Fe^+).

Specimens were therefore etched, as described above, and the resultant rosettes examined (see Fig. 2). The rosettes on the unimplanted specimens were well-formed with individual dislocation etch pits easily visible (Fig. 2a). These rosettes consisted almost entirely of the traces of the $\{1\,1\,0\}_{90}$ planes. Those on the implanted specimens were rather ill-formed, for all doses used; the etched area appeared to have linear, rather than point, features. SEM examination showed the differences in etching behaviour more clearly (Figs 2c, d). The surface ripples seen in the implanted specimen are probably due to a large number of dislocation loops ending in the disordered surface layer. The short rosette arms in the <1 0 0> directions, visible on the unimplanted specimens, could not be seen on the implanted specimens.

While the ends of the rosette arms in the implanted specimen are not very well defined, it appears that the rosettes in the implanted specimens are (if there is any genuine change) only slightly shorter than those in the unimplanted specimens. This is in contrast to the results of Burnett and Page [7] for implanted MgO. It should be noted, however, that MgO and LiF, though having the same crystallography of slip, differ in several respects in the patterns of slip seen around indentations. The "troughing" observed by Keh [25] and Armstrong and Wu [26] along <1 0 0> directions in MgO is absent, rather "pile-up" can be seen (Fig. 2c) around indentations in LiF. This is associated with the predominance of slip on $\{1\,1\,0\}_{90}$ planes in LiF, compared to the dominant $\{1\,1\,0\}_{45}$ planes in MgO, and may be related to the different homologous testing temperatures of the two materials. Thus, Brookes *et al.* [27] have observed changes in hardness anisotropy behaviour in MgO, LiF and NaCl which are possibly connected with the activation of secondary {1 0 0} <0 1 1> slip at higher homologous temperatures. Additionally, the ion species selected by Burnett and Page [7] for implantation into MgO were selected for a high probability of resultant surface hardening; this would not necessarily be expected to occur for the case of nitrogen implantation into LiF.

3.3. Indentation fracture

Indentations in unimplanted LiF showed no fracture, even at the highest loads used. In contrast, indentations in implanted material, even at the minimum load (5 g) and dose ($2 \times 10^{17}\,cm^{-2}$) used, showed radial cracking. The cracks extended along <1 0 0> directions from indentation corners; some low-load indentations also showed cracks along <1 1 0>. If the crack planes are normal to the surface this would imply that fracture is on {1 0 0} and {1 1 0} planes). Crack sizes were measured and the results are shown in Table II.

It is unlikely that implantation affects simply the

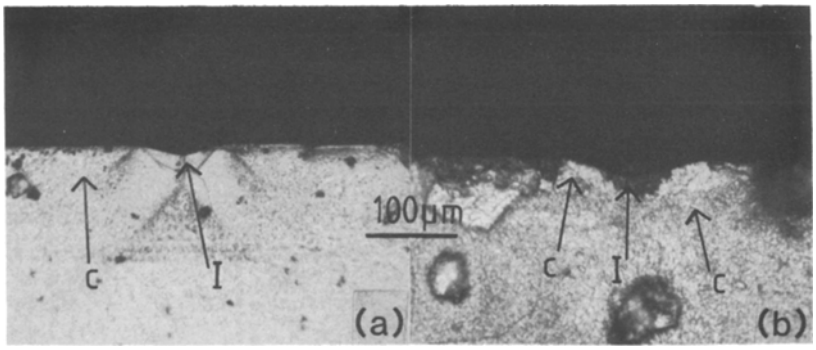

Figure 3 Reflected light micrographs of cross-sectioned 200 g indentations in LiF implanted to $2 \times 10^{17}\,cm^{-2}$, after etching. Cracks (C) are visible (in plan) close to the surface on either side of the indentation (I). The cracks are shallow and appear to have nucleated separately on either side of the indentation.

crack growth, since no cracks were observed even at the highest loads on unimplanted LiF. Implantation must therefore alter the crack nucleation. There are two possible reasons for this:

(i) cracks nucleating below the surface: the stress state associated with implantation is predominantly in-plane compression at the surface [9, 28], but may have tensile and shear components at greater depths, which might promote crack nucleation;

(ii) cracks nucleating at the surface: in this case cracking might be promoted if implantation damage provides crack nuclei and/or if the implanted material has a lower fracture toughness than normal LiF.

To distinguish between these two possibilities, attempts were made to cross-section specimens through indentations, by cleavage through a row of indentations. However, there was a strong tendency for specimens to fracture along random {1 0 0} planes rather than through the indentations; only one specimen (dose $2 \times 10^{17}\,cm^{-2}$) was successfully prepared. Examination of this specimen (see Fig. 3) suggested that surface nucleation of cracks had occurred (independently) on each side of the indenter. This supports the suggestion that implanted LiF has a lower fracture toughness than unimplanted LiF, and/or that implantation damage provides crack nuclei.

4. Implanted and X-irradiated LiF

Ion implantation would be expected to produce some displacement damage even at depths very large compared to the mean ion range. Therefore, some implanted specimens (dose $6 \times 10^{17}\,cm^{-2}$) were subsequently X-irradiated so as to investigate the possible interactions of displacement and ionization damage. Unimplanted specimens were also X-irradiated.

The specimens were mounted on a slotted lead sheet so that a region approximately 3 mm in width was exposed to the X-ray beam. The implanted specimens were oriented with the implanted side facing the beam. The radiation used was Cr$K\alpha$ (wavelength = 0.229 nm) from a Siemens Sequential X-ray spectrometer fitted with a Kristalloflex 4 source operating at 50 kV and 40 mA. Exposure was for 7 h.

Initial examination of the samples showed a surprising difference between the pre-implanted and the normal LiF (see Fig. 4). The unimplanted specimens were dark brown in colour only near to the exposed surface, fading rapidly to yellow over a depth of ~1 mm. However, the implanted specimens were dark throughout their thickness, with only a slight attenuation in colour with depth.

Since such strong colour effects were produced, it was decided to investigate the hardness of implanted/irradiated specimens in cross-section. Rosette sizes could then easily be measured as all tests would be carried out on crystalline material. Crystals were cleaved normal to the irradiated surface. Indentations were made at a load of 25 g in a line that traversed the irradiated zone at constant depth (75 μm) and in a line going into the depth of the crystal. Results of the hardness measurements are shown in Fig. 5. It can be seen that pre-implanted and unimplanted specimens are indistinguishable in their hardness behaviour.

The specimens were then etched and the rosette sizes measured. Data from indentations to a depth of 1 mm are shown in Fig. 6. It can be seen that the

TABLE II Crack lengths in implanted LiF

Indenting load (g)	Indentation diagonal (μm)	Crack length (μm)
200	59 ± 2	140 ± 20
100	40 ± 2	90 ± 10
50	30 ± 1	50 ± 5
25	20 ± 1	41 ± 5

Crack lengths are total end-to-end lengths, including the indentation diagonal.

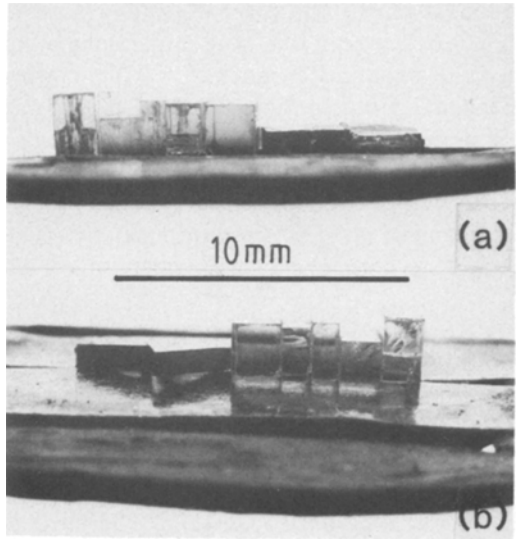

Figure 4 Macrophotographs of X-irradiated LiF. The thinnest two specimens (far right in (a)) were pre-implanted to $6 \times 10^{17}\,cm^{-2}$; these specimens are dark throughout. The unimplanted LiF specimens show a rapid decrease in colour density with depth.

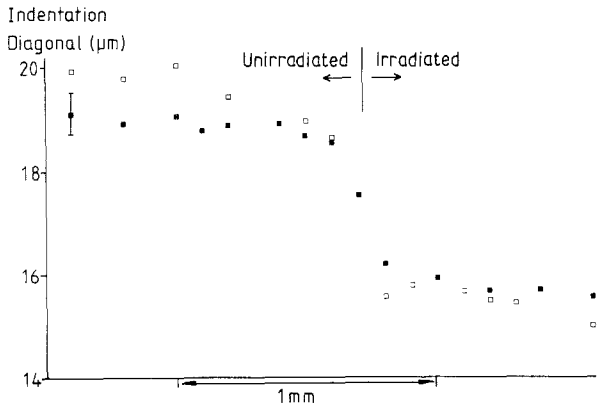

Figure 5 Sizes of 50 g indentations, made at 75 μm depth, crossing the unirradiated/irradiated boundary. No significant differences can be seen between unimplanted and implanted LiF. (■) Unimplanted and (□) implanted X-irradiated LiF.

rosettes in the pre-implanted specimens are consistently smaller than those in the unimplanted specimen, but that the difference is small except within $\sim 150 \mu m$ of the specimen surface. This depth is still ~ 300 times that of the peak ion range, but is comparable with the X-ray attenuation distance. (Note that on this figure, each data point corresponds to only two measurements; errors are therefore difficult to estimate. However, the consistency of the linear parts of the curves indicate errors of $\sim \pm 5 \mu m$.)

These observations can probably only be attributed to the effects of ion channelling [14]. While only a very small fraction of the incident nitrogen would be expected to be near the channelling orientation, it would appear that enough are channelled to produce vacancies, etc. deep inside the crystal. Subsequent ionization damage by X-rays still produces a visibly high density of colour centres, at considerable depths, even after X-ray absorption. The changes in rosette size at depths up to 1 mm in the pre-implanted specimens are much less marked than the changes in colour. This indicates that the colour centres inhibiting dislocation motion are not exclusively (or primarily) those causing the visible colour change, as has been reported for NaCl (e.g. [29].

5. Conclusions

The results given in more detail and discussed above may be summarized as:

1. Ion implantation alone, up to doses of $6 \times 10^{17} N_2^+ cm^{-2}$ does not affect the microhardness or (probably) the rosette sizes on the implanted surface.
2. Implantation produces microstructural changes in the surface that alter the etching behaviour.
3. Either implantation damage provides crack nuclei, or the implanted surface has a lower fracture toughness than the normal material.
4. Pre-implanted X-irradiated specimens show an enhanced reduction in rosette size in the irradiated zone, compared with unimplanted irradiated samples. Thus implatation gives rise to latent hardening centres activated by ionization during X-irradiation. The effect persists to a depth of $\sim 150 \mu m$.
5. Colour centres in the X-irradiated zone persist to a far greater depth in the pre-implanted specimens. This effect is probably due to the channelling of a small fraction of the incident ions.

Acknowledgements

The work described here was supported by an SERC CASE award, in collaboration with UKAEA Harwell (Ion Implantation Group). Implantations were performed with the assistance of G. Dearnaley and G. Proctor. Laboratory facilities in Cambridge were provided by Professor R. W. K. Honeycombe, F Eng, FRS.

References

1. G. DEARNALEY, *Mat. Eng. Appl.* **1** (1978) 28.
2. S. G. ROBERTS, PhD thesis, University of Cambridge, (1983).
3. S. G. ROBERTS and T. F. PAGE, in "Ion Implantation into Metals", edited by V. Ashworth, W. A. Grant and R. P. M. Procter (Pergamon, Oxford, 1982) p. 135.
4. *Idem, J. Mater. Sci.* **21** (1986) 457.
5. P. J. BURNETT and T. F. PAGE, *ibid.* **19** (1984) 845.
6. *Idem*, ibid. **19** (1984) 3524.
7. *Idem, Proc. Mat. Res. Soc.* **27** (1984) 401.
8. *Idem*, Proceedings of the Conference "Science of Hard Materials II", Rhodes, Greece, September 1984, edited by E. A. Almond, C. A. Brookes and R. Warren, Institute of Physics Conference Series, Vol. 75 (Adam Hilger, Bristol, 1986) p. 789.
9. *Idem, J. Mater. Sci.* **20** (1985) 4624.

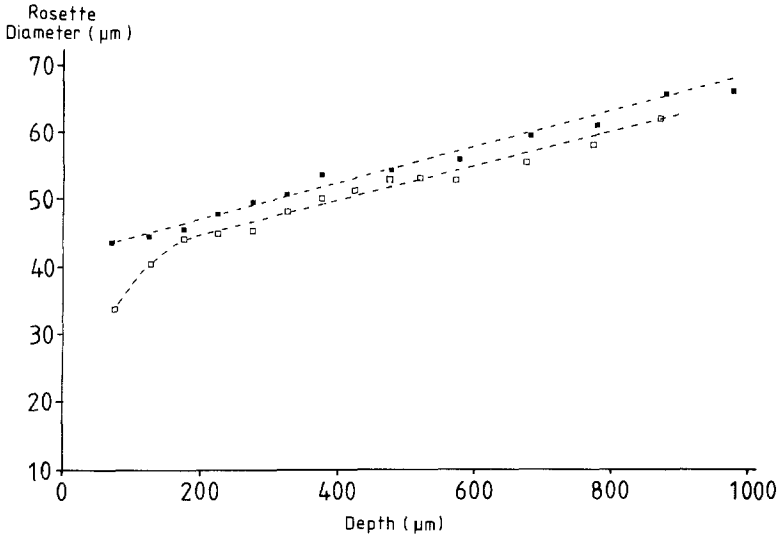

Figure 6 Variation of rosette size (50 g indentations) with depth for (■) unimplanted and (□) pre-implanted X-irradiated LiF. Close to the surface, rosettes are smaller in pre-implanted material.

10. C. KITTEL, "Introduction to Solid State Physics" (Wiley, New York, 1976).
11. A. D. WHAPHAM, *Phil. Mag.* **3** (1957) 103.
12. C. R. A. CATLOW, K. M. DILLER and L. W. HOBBS, *ibid.* **42a** (1980) 123.
13. T. E. MITCHELL and A. H. HEUER, *Mat. Sci. Eng.* **28** (1977) 81.
14. G. CARTER and W. S. GRANT, "Ion Implantation of Semiconductors" (Edward Arnold, London, 1976).
15. C. H. MACGILLAVRY and G. D. RIECK (eds), "International Tables for X-ray Crystallography", Vol. III (Kynoch, Birmingham, 1962).
16. J. J. GILMAN and W. J. JOHNSTON, in "Dislocations and the Mechanical Properties of Crystals", edited by J. C. Fisher, W. G. Johnston, R. Thomson and T. Vreeland (Wiley, New York, 1957) p. 116.
17. B. J. HOCKEY, in "The Science of Hardness Testing and its Research Applications", edited by J. H. Westbrook and H. Conrad (American Society for Metals, Ohio, 1973) p. 21.
18. P. M. SARGENT, PhD thesis, University of Cambridge (1979).
19. G. PROCTOR, UKAEA Harwell, private communication (1980).
20. C. A. BROOKES, J. B. O'NEILL and B. A. W. REDFERN, *Proc. Roy. Soc.* **A322** (1971) 73.
21. S. J. BULL, University of Cambridge, private communication (1985).
22. I. MANNING and G. P. MUELLER, *Comp. Phys. Commun.* **7** (1974) 85.
23. P. M. SARGENT and T. F. PAGE, *Proc. Brit. Ceram. Soc.* **26** (1978) 193.
24. P. J. BURNETT and T. F. PAGE, submitted to *Proc. Roy. Soc.*
25. A. S. KEH, *J. Appl. Phys.* **31** (1961) 1538.
26. R. W. ARMSTRONG and C. C. WU, *J. Amer. Ceram. Soc.* **61** (1978) 102.
27. C. A. BROOKES, R. P. BURNAND and J. E. MORGAN, *J. Mater. Sci.* **10** (1975) 2171.
28. E. P. EERNISSE, *Appl. Phys. Lett.* **18** (1971) 581.
29. I. S. LERMA and F. AGULLO-LOPEZ, *Phil. Mag.* **27** (1973) 993.

Received 30 January
and accepted 14 March 1986