

## 22.—Influence of Colour Centres on the Plastic Deformation of Halide Crystals

By C. DUPUY and B. SCHAEFFER  
*Laboratoire de Minéralogie et Pétrographie,  
Faculté des Sciences, Strasbourg.*

### ABSTRACT

*Mechanical properties of gamma-irradiated and then annealed LiF crystals were examined. In compression tests, small deformations nucleate single glide bands which widen into highly sheared deformation bands with sharp yield drops in the load/elongation curve. Interaction between dislocations and colour centres was evidenced by luminescence and dichroic colour change in the deformation bands. Xerographic and electrometric methods were used to investigate the deformation-induced electrical charges. They were found to be of opposite signs in irradiated and in as-grown crystals. Electrical signals corresponding to single glide bands were recorded. The charges are interpreted in terms of vacancies drawn by dislocations.*

### 1. INTRODUCTION

The effect of gamma-irradiation on the yield stress of LiF crystals has been extensively studied by NADEAU and JOHNSTON.<sup>1</sup> They investigated the variations in the colour centre densities during pulse-annealing of irradiated crystals as well as the corresponding yield stress.<sup>2</sup> We used this method as a convenient tool to produce a continuous variation in the mechanical properties from brittleness to ductility. Radiation hardening made it possible to measure the residual stresses produced by bending in LiF.<sup>3</sup> Coloured LiF crystals show mechanical properties very similar to those observed in MgO.<sup>4,5</sup> The growth of single glide bands could be followed. This results in a great simplification in the photoelastic study of the stresses developed by the dislocations<sup>6</sup> as well as in the investigation of the charges they bear. The problems raised by the intersection of glide bands are avoided.

### 2. EXPERIMENTAL PROCEDURES

Large blocks from Harshaw were irradiated in a cobalt-60 gamma-ray source (10<sup>7</sup>R). After cleavage along {100} planes, samples

( $25 \times 4 \times 3$  mm.) were annealed at  $280^\circ\text{C}$ . A red and then an orange colour were observed. The quantitative study of the colour centres has not yet been carried out. In order to localize the plastic deformation, the samples were annealed only in their central part,<sup>7</sup> using a few turns of a resistant wire.

The samples were deformed by compression and in four-point bending with an Instron testing machine at speeds of 5 or  $50\mu\text{m}/\text{min}$ . A vertically and horizontally movable optical bench was mounted on the machine. The bench carried an horizontal polarizing microscope enabling the specimen to be observed during deformation. Both photographic and cine-camera methods could be used. The electrical charges appearing during deformation were visualized by means of a xerographic method.<sup>8</sup> The values of the charges were measured with a vibrating-reed electrometer, as described in the literature.<sup>9,10</sup>

### 3. PHOTOELASTIC STUDY

Irradiated LiF crystals show a high yield stress (increase from 1 to  $7\text{ kg}/\text{mm}^2$  is produced by irradiation); the photoelastic study is easier than in as-grown samples in which the first glide bands are scarcely detectable. The yield stresses in coloured crystals being higher, the stresses due to dislocations are also higher and consequently the contrast along the glide bands is sharper.

#### 3.1 Isolated Slip Bands

It was possible to obtain only one slip band in coloured samples (Figure 1). A very small plastic deformation was given to the sample with a "hard" machine. The applied force was suppressed immediately after the first glide band had appeared in the central part of an irradiated sample where the yield stress was reduced down to  $2\text{ kg}/\text{mm}^2$  by annealing.

Birefringences of opposite signs, corresponding to tensile and compressive regions, are observed on each side of the glide band, separated by a black line. These birefringences show a minimum along the glide plane, at a point we shall call S, at the right of the sample. This pattern is interpreted in terms of dislocations, as shown on Figure 5B. Dislocation sources are assumed to be located on the line SS' (Figure 5A).<sup>11</sup> A more detailed study is given elsewhere.<sup>6</sup> The dislocation sources are not equidistant from faces (100) and ( $\bar{1}00$ ), as was observed by MENDELSON;<sup>12</sup> buckling occurred during the compression test. The dislocation sources are shifted towards the face ( $\bar{1}00$ ), where the yield stress was reached first. The distance from face ( $\bar{1}00$ ) varies from 0.1 to 1 mm with decreasing colour centre

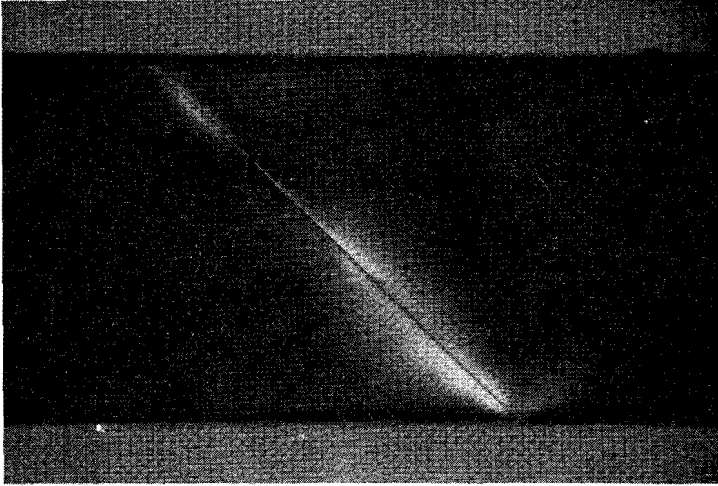


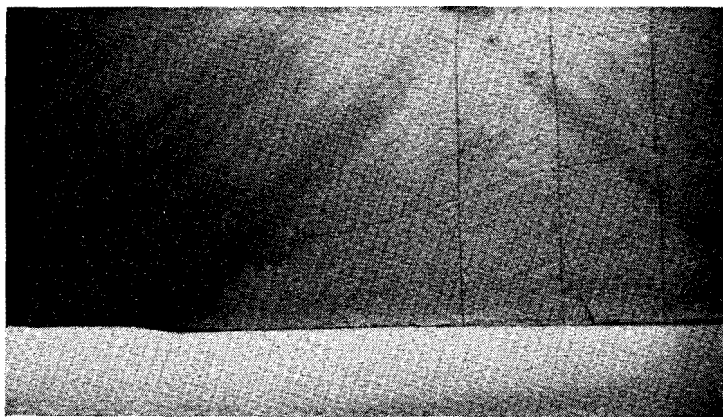
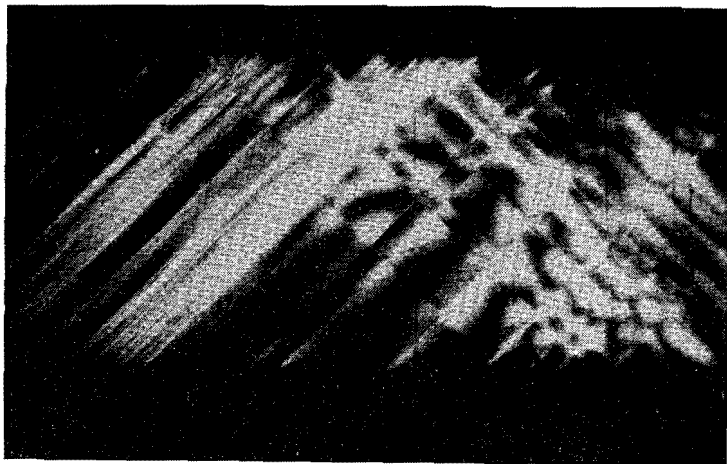
FIGURE 1.—Residual stresses in coloured LiF due to dislocations piled up in a single glide band. The nicols are crossed parallel to the edges of the figure.

density. This buckling is due to a non-uniformity of the stress and, moreover, the yield stress, owing to the method of annealing of the samples, is not uniform across the gauge section. Observation did not show if slip nucleated at S or at the surface, but it seemed that dislocations started from S as soon as the source was observable. Two slip steps appeared, a first one near S, on face  $(\bar{1}00)$  and, then, a second one, on face  $(100)$ , as the glide band reached it. Afterwards, the long-range stresses were progressively released and the glide band appeared as a thin birefringent lamella similar to that described by ARGON and OROWAN.<sup>4</sup> No other slip band was detected during this process.

### 3.2 Deformation Bands

As deformation proceeds, new glide bands are formed adjacent to the first one in a few seconds, independently of machine speed, producing sharp yield drops on the load/elongation curve.

A highly deformed sample, prepared in the same manner as described above, is shown in Figure 2. The temperature during annealing was not uniform; bleaching was stronger in the central part of the sample at the right hand side, where the temperature was maximum. The glide bands appeared first in the clearer region, where the yield stress was minimum (Figure 3). Unusual high deformations, which



FIGURES 2 and 3.—Glide bands in coloured LiF.  
 (Upper.) 2. Crossed nicols, parallel to the cube edges.  
 3. Polarizer only; the orientation of its vibration is horizontal.

cannot be obtained with colourless samples, corresponding to a shear angle of  $14^\circ$ , were observed in the deformation bands.

#### 4. OPTICAL EFFECTS ASSOCIATED WITH GLIDE BAND FORMATION

Observation of the deformed samples show that glide bands appear darker. F or M centres seem to be captured by dislocations, creating

anisotropic centres oriented approximately perpendicularly to the compression axis.

Light-emission occurred along the glide planes during deformation and was photographed (Figure 4). This luminescence seems to be related to destruction or transformation of colour centres. As SEITZ pointed out, electrons or holes evaporate and have an opportunity to recombine when dislocations pass very close to the colour centres.<sup>13</sup>

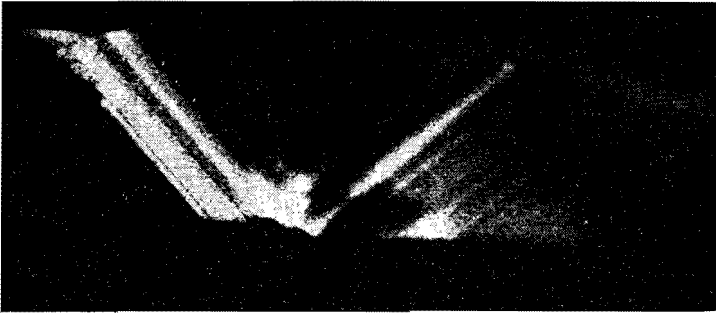


FIGURE 4.—Deformation-induced luminescence along glide bands.

## 5. INFLUENCE OF COLOUR CENTRES ON ELECTRICAL CHARGES PRODUCED DURING PLASTIC FLOW OF LiF

It will be easier to study the effect of colour centres on the electrical charges appearing during deformation on samples containing only a few glide bands. The dislocation distribution is simplified and can be recognized easily from the photoelastic pattern; a comparison is possible between the edge dislocation distribution and the charge distribution. The resultant charge of many glide bands will be obtained by superposing the charge distributions of the individual glide bands.

### 5.1 Charge Distribution on an Isolated Glide Band of a Coloured Sample

The xerographic method used previously<sup>8</sup> was developed by using a mixture of red lead and sulphur powder.<sup>14</sup> It is a sensitive tool for studying the electrical charges produced on a single glide band. Line  $SS'$  (Figure 5) separates regions of the glide band containing excess of dislocations of positive and negative mechanical signs. Concentrations of red lead are observed on  $S$  and  $S'$  (Figure 6B), therefore dislocation sources are negatively charged. Negative charges are also observed along the slip step on face  $(\bar{1}00)$  (Figure 6C). The

opposite step, on (100), of the glide band is positively charged; a line of sulphur is visible on Figure 6A. The corresponding dislocation distribution is schematized in Figure 5B.

The same signs for the electrical charges are found with the electrometer. Electrodes were painted on faces (100) and  $(\bar{1}00)$ ; the corresponding signals were respectively positive and negative. The values of the signals correspond to  $10^8$  electronic charges for one glide band.

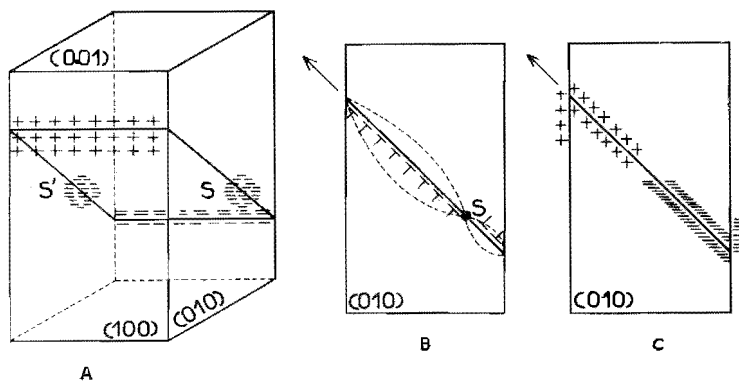
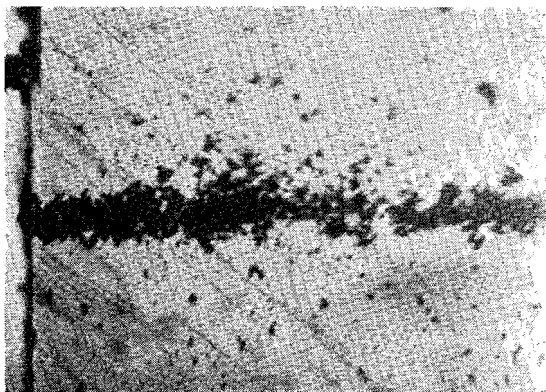


FIGURE 5.

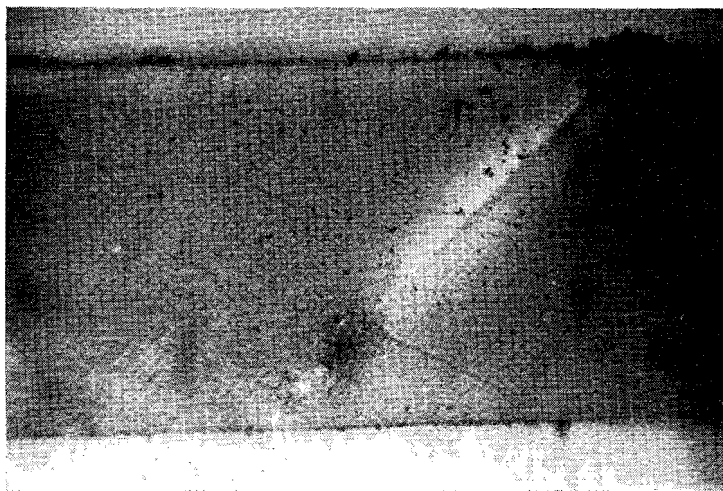
- A. Charge distribution along the glide plane.
- B. Edge dislocation distribution in the glide plane (compare Figure 1). The glide band moved in the direction of the arrow.
- C. Charge distribution on the (010) face in the second stage, when long-range stresses are released.

During the second stage, many dislocation sources are produced; again, the photoelastic observations show that dislocation sources coincide with accumulations of red lead powder on faces  $(\bar{1}00)$  and (100) (Figure 5c). However, the accumulations of red lead are only observed on the right part of the glide band; heaps of sulphur are observed on the left side. Now the glide band appears as a belt around the crystal, the right half being negatively charged and the left one positively charged. When deformation bands are formed, the distribution is the same, but the belt is wider.

These experiments show that dislocation sources detected by the photoelastic method are negatively charged in coloured LiF crystals. Positive charges should be carried by edge dislocations; in fact, only the slip step on face (100) is observed to be positively charged. The



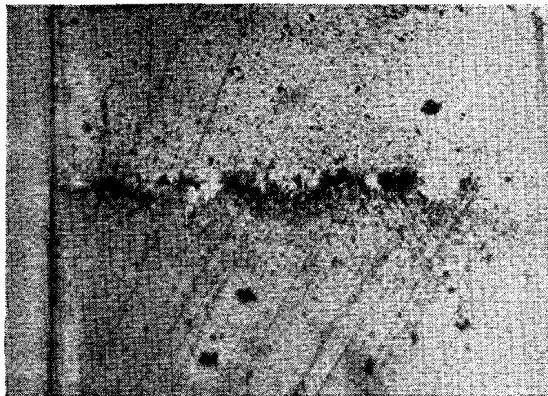
A



B

FIGURE 6.

- A. Sulphur line fixed on (100).  
B. Concentration of red lead powder around the dislocation source (polarized light).



c

FIGURE 6.—continued  
c. Red lead fixed on  $(\bar{1}00)$ .

absence of sulphur powder on the slip step on face  $(\bar{1}00)$  is likely due to the effect of the negative space charge on  $SS'$ .

## 5.2 Study of Colourless Samples

The observation of isolated glide bands is more difficult in colourless crystals, since many glide bands appear simultaneously. However, it was possible to confirm the results obtained with coloured samples: dislocations now carry negative charges, while sources are positively charged. The sign of the charges is reversed by gamma irradiation, confirming the results obtained by DAVIDGE<sup>15</sup> and DEKEYSER.<sup>16</sup>

The values of the charges produced during deformation, measured with the electrometer were, for 1% strain, of the order of  $10^8$  electronic charges per square millimeter of one electrode. The thickness of the sample was 3 mm and the yield stress was 1.2 kg/mm<sup>2</sup>.

## 5.3 Bending-tests

In pure bending, the crystal is divided into two parts by the neutral plane. A xerographic study of irradiated crystals shows that the upper and lower faces are both negatively charged. The sources  $S_c$  and  $S_t$  (Figure 7A) are negatively charged; positive charges appear on the neutral plane. A negative signal is recorded on each electrode painted on faces  $(001)$  and  $(00\bar{1})$ . Opposite signs for the charges are again found in colourless crystals.



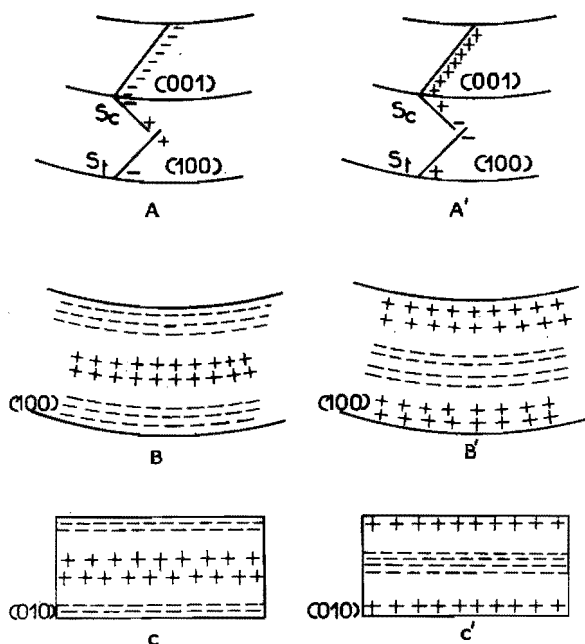


FIGURE 7.—Comparison of charge distribution in bending for irradiated (A, B, C) and annealed (A', B', C') crystals.

A, A' Isolated bands.

B, B' Important deformation distribution on the side faces of the specimen.

C, C' Distribution on a (010) cleaved face of a highly bent specimen.

A sharply bent crystal was cleaved and then the mixture of red lead and sulphur was blown on to the cleavage face. Red lead particles were fixed on the neutral plane and sulphur towards the upper and lower surfaces (Figure 7C'). This experiment confirms that the charges produced during deformation are distributed throughout the whole volume of deformed crystal.

## 6. DISCUSSION

The results obtained with the xerographic method are consistent with the model described by WHITWORTH,<sup>10</sup> at least in the case of bending. Charges of opposite signs appear on opposite faces during compression experiments, but this is understandable if one admits that plastic buckling occurs. Our experiments showed that, especially in coloured samples, the charge distribution, like the dislocation distribution, is very sensitive to asymmetric strains.

The xerographic method, though of a qualitative nature, is able to visualize the detailed topography of the charges formed during the deformation on or below the surface. A charged particle does indeed stick at a point where the electric field of all the charges in the crystal is attractive. However, the electric field due to charges at a large distance from the point of impact is generally negligible compared with the field of the charges in its vicinity. An estimate of the distance at which particles may be attracted is given by the size of the pattern around S (Figure 6B). Almost all the particles are fixed in a circle of radius 0.5 mm. Care must be taken when charges of both signs are neighbouring, which occurs near the face (100) where a complicated pattern (Figure 6C) is observed. Particles are only fixed where the influence of the dislocation sources is preponderant and no particles are fixed where the charges carried by the dislocations have appeared.

The mechanism of charge transport is not yet clear. WHITWORTH<sup>18</sup> showed that charges may be transported by jogs or vacancies. It is possible to give an interpretation in terms of vacancy migration. Metal ion vacancies, due to positive divalent impurities, are always present, even in nominally pure crystals, and may move with the dislocations; these will be negatively charged. During gamma irradiation, F and H centres are formed;<sup>19</sup> these centres may be destroyed by dislocations. Electrons are freed and then retrapped on the H centres, creating halogen interstitials. Halogen vacancies from the F or F aggregate centres may glide with the dislocations and charge them positively if the F centres are more numerous than the metal ion vacancies.

#### ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to Professors H. Curien, W. Dekeyser, and H. Saucier for helpful discussion. Gratitude is also expressed to Mademoiselle C. Baltzinger for irradiating the crystals, and to Professor B. W. Low for her suggestions in the preparation of the English manuscript. This work was supported, in part, by the Commissariat à l'Énergie Atomique.

#### REFERENCES

1. NADEAU, J. S., and JOHNSTON, W. G., *J. Appl. Phys.*, **32**, 2563, 1961.
2. NADEAU, J. S., *J. Appl. Phys.* **33**, 3480, 1962.
3. DUPUY, C., SAUCIER, H., and SCHAEFFER, B., *C. R. Acad. Sci. Paris*, **257**, 4170, 1963.
4. ARGON, A. S., and OROWAN, E., *Phil. Mag.*, **9**, 1003, 1964.
5. TATTERSAL, H. G., and CLARKE, F. J. P., *Phil. Mag.*, **7**, 1977, 1962.
6. SCHAEFFER, B., DUPUY, C., and SAUCIER, H., *Phys. Stat. Sol.* **9**, 753, 1965.
7. CRUSSARD, C., *Mém. Scient. Rev. Mét.*, **61**, 231, 1964.

8. SAUCIER, H., and DUPUY, C., *C. R. Acad. Sci. Paris*, **252**, 1039, 1961.
9. HIKATA, A., ELBAUM, C., CHICK, B., and TRUELL, R., *J. Appl. Phys.*, **34**, 2154, 1963.
10. WHITWORTH, R. W., *Phil. Mag.*, **10**, 801, 1964.
11. KEAR, B. H., and PRATT, P. L., *Acta Met.*, **6**, 457, 1958.
12. MENDELSON, S., *J. Appl. Phys.*, **32**, 1999, 1961.
13. SEITZ, F., *Phys. Rev.*, **80**, 239, 1950.
14. KUNDT, A., *Sitzungsber. Akad. Wiss. Berlin*, **16**, 5 April, 1883.
15. DAVIDGE, R. W., *J. Phys. Chem. Solids*, **25**, 907, 1964.
16. DEKEYSER, W. Private Communication.
17. DUPUY, C. H. S., SCHAEFFER, B., and SAUCIER, H., *C. R. Acad. Sci. Paris*, **260**, 4481, 1965.
18. WHITWORTH, R. W., *Phil. Mag.*, **11**, 83, 1965.
19. NADEAU, J. S., *J. Appl. Phys.*, **35**, 1248, 1964.