LETTER TO THE EDITOR

Dislocation stimulated orientation of colour centres in cubic crystals

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Abstract. The centres generated by a moving dislocation retain their orientation when the dislocation moves away from them. The dichroism in the plastically deformed crystals might, therefore, be due to the alignment of point defects and not to the dislocations themselves. It is shown that the different dislocations forming the slip band cause the same orientation of point defects. The splitting of the creation energy of the centres due to the dislocation elastic field is considered. An expression is obtained to determine the orientation of the centres when the slip system is known. This approach is applied to the experimental results on the N_c band dichroism in LiF crystals which have been deformed after γ-irradiation.

The orientation of point defects in cubic crystals can cause optical anisotropy. It can also arise via bleaching with polarised light, causing the reorientation of the colour centres (Okamoto 1961). Plastic deformation is also known to produce dichroism in cubic crystals (Serughetti *et al* 1967, Basiev *et al* 1986, Stepanov and Shirokov 1987). The latter case is more difficult to understand, since dislocation debris might contain both point centres and more complex anisotropic imperfections. The alignment of point defects by plastic deformation is considered in this letter.

The orientation of centres by dislocations certainly does not cause the macroscopic crystal anisotropy, since small regions with point defects aligned in different directions might compensate each other. Our considerations show the conditions under which moving dislocations of various types cause the orientation of all centres in one direction. This is the case when the centres are created in the wake of the moving dislocations, that is behind them close to their glide planes.

The present approach enables one to find the orientation of centres by deformation when the slip system is known. This approach is applied to account for dichroic absorption of the deformed LiF crystals in the 550 nm spectral region. We also discuss the conditions necessary for such effects to take place in other crystals.

When the γ-irradiated LiF crystals are compressed along the [001] direction, one ((001), [0$\bar{1}$1]) or two ((011), [0$\bar{1}$1] and (0$\bar{1}$1), [0$\bar{1}\bar{1}$]) slip bands are developed (see figure 1). The weak absorption band at about 550 nm arises in the deformed regions of the sample in addition to the M and R spectral bands observed before deformation (figure 2). The deformation induced band is close to the N_c band known to arise as a result of the R light bleaching (Van der Lugt and Kim 1968). The latter in turn looks like the N_2 band which is generated by thermal annealing. This gave rise to the question (Van der Lugt and Kim 1968, Kamikawa and Ozawa 1969) of whether the 550 nm bands produced
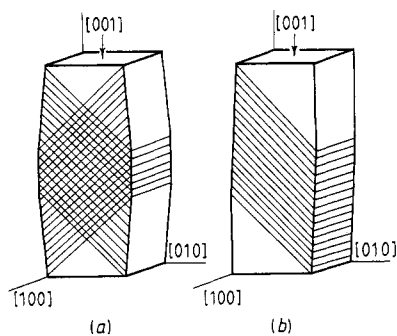
Figure 1. Reference frame for the deformed LiF crystals with (*a*) one and (*b*) two slip bands.
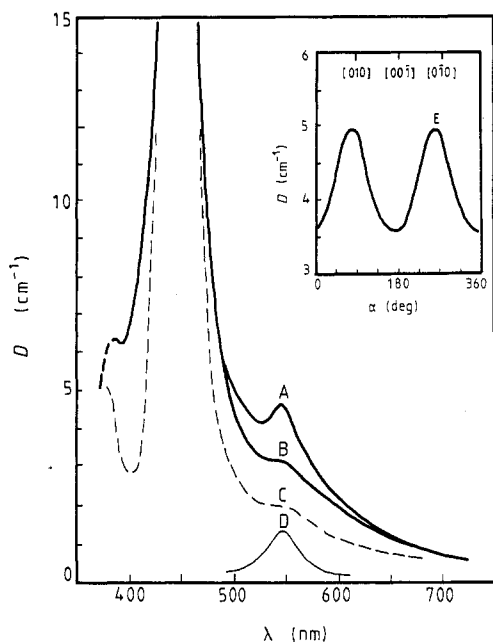

Figure 2. Absorption spectra of the plastically deformed LiF crystals (7% deformation) in polarised light. A: [010] polarisation for light travelling along [100]; B: [001] polarisation for light travelling along [100] and any polarisation for light travelling along [010]; C: absorption spectrum of the sample before deformation; D: difference betwen the spectra A and B; E: angular dependence of 550 nm absorption, the sample rotating round the light travelling direction [100].

by different treatments correspond to the same centre. We have shown that the parameters of such bands coincide precisely, regardless of the history of the sample—see table 1. It was concluded that the N_c centres, produced by thermal, optical or mechanical actions, are identical (Stepanov 1989).

The deformation induced band is dichroic. The polarisation of absorption lies perpendicularly to the direction of the compression (Serughetti *et al* 1967), along the sample's expansion direction, [010] (Basiev *et al* 1986). The slip band is induced by shear stress rather than by compression and the centres behave in the same way (Stepanov 1988). When the sample is immersed in an electrolyte solution to remove the electrostatic self-charging by deformation, its optical properties are the same as if it were deformed in air. The plastically deformed sample is annealed with a heating rate of 4 K min^{-1}. At about 450 K the 550 nm dichroism disappears. When the crystal is γ-irradiated after plastic deformation, no dichroism arises in the 550 nm region.

Table 1. Spectral parameters of the N_c bands generated by different actions.

Parameter	$N_c(UV)$†	$N_c(T)$‡	$N_c(PD)$§
λ (nm) (293 K)	549.8 ± 0.4	549.7 ± 0.2	549.6
$\delta\lambda$ (nm) (293 K)	18.0 ± 0.5	18.1 ± 0.5	17.0
λ (nm) (77 K)	541.3 ± 0.2	541.5 ± 0.5	541.8
$d\lambda/dp$ (nm GPa^{-1})	-0.063 ± 0.001	-0.066 ± 0.002	
Dipole direction	$\langle 001 \rangle$		$\langle 001 \rangle$

† After UV bleaching.
‡ After 450 K annealing.
§ After 7% plastic deformation.

The R light induced N_c band does not display optically stimulated dichroism (Van der Lugt and Kim 1966). According to our experimental data, these centres are not influenced by an electric field up to 30 kV cm^{-1} acting during the R bleaching or after it. We did not succeed in orienting the previously formed centres by applying [001] elastic compression. However, if the R light and the [001] elastic compression act simultaneously, the N_c band being created does show slight dichroism, the centres preferring the compression direction. The polarisation degree rises as the first power of the applied field, the proportionality factor being 0.01 mm^2 kG^{-1} (Stepanov 1988). When the previously deformed samples are bleached with the R light, the strong isotropic N_c band arises, the dichroic part of the absorption induced by the deformation remaining unchanged. The formation rate of the N_c centres is close to that in undeformed crystals.

The main point of the present consideration is that the centres produced by deformation are situated in thin layers behind the dislocations. This is not a novel idea (see Senchukov and Shmurak 1970, Clark and Crowford 1973) but when applied to the local elastic field it produces a remarkable result.

Suppose a dislocation with the tangential vector l and Burgers vector b defined with a plus sign according to Friedel (1964)

$$b = + \oint dU \tag{1}$$

moves in the glide pane in the u direction, $l \cdot u = 0$. We define the normal to the plane, n, as

$$n = l \times u. \tag{2}$$

Hence vectors $\{l, u, n\}$ form the frame of reference bound to the dislocation. Since only dislocation gliding is considered, $b \cdot n = 0$ and b is represented by

$$b = lb_s + ub_e \tag{3}$$

where $b_s = l \cdot b$ and $b_e = u \cdot b$ are the screw and the edge components of b. In the dislocation train (the negative u direction) the only non-vanishing components of the elastic strain tensor, σ_{ij}, caused by the edge and the screw components of the dislocation are given with respect to $\{l, u, n\}$ by

$$\sigma_{23}^e = -[\mu b_e / 2\pi(1 - \nu)]/R \tag{4a}$$

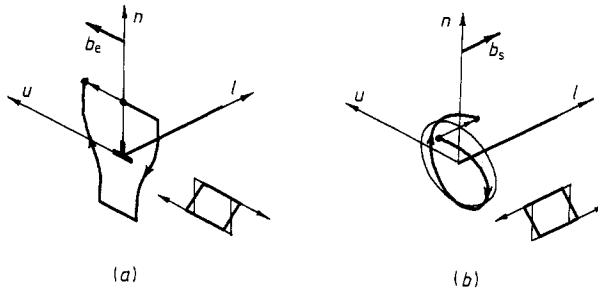$$\sigma_{13}^s = -(\mu b_s / 2\pi)/R. \tag{4b}$$

Figure 3. The dislocation frame of reference. The lattice distortion caused by the edge (*a*) and the screw (*b*) dislocations.

R is the distance from the dislocation, ν the effective Poisson ratio. Figure 3 shows the variables in (4).

The definitions (1) and (2) are adopted so that the displacement of the 'upper' part of the crystal, indicated by the n vector, is b when the dislocation moves through the crystal. We will introduce the 'macroscopic' frame of reference

$$e_1 = t \times n \qquad e_2 = t \qquad e_3 = n \tag{5}$$

where t is the unit displacement vector

$$t = b/b. \tag{6}$$

Macroscopic plastic deformation with respect to $\{e_1, e_2, e_3\}$ is given by

$$u_{ij}^{\text{macro}} = \tfrac{1}{2}\alpha(t_i n_j + t_j n_i) = \tfrac{1}{2}\alpha \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{7}$$

where $\alpha > 0$ is the degree of deformation. The conversion matrix from the $\{l, u, n\}$ to the $\{e_1, e_2, e_3\}$ frame of reference is

$$A = \frac{1}{b} \begin{bmatrix} -b_e & b_s & 0 \\ -b_s & b_e & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{8}$$

From (4) and (8) we now get the equation for the dislocation train elastic field with respect to the macroscopic $\{e_1, e_2, e_3\}$ reference frame:

$$\sigma_{ij}^{\text{disl}} = -\frac{\mu b}{2\pi(1 - \nu)R} \left(1 - \nu \frac{b_s^2}{b^2}\right) \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} - \nu \frac{b_s b_e}{b^2} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}. \tag{9}$$

The second term vanishes for the pure screw and edge dislocations. For mixed ones it is small, since ν is not large for most of the crystals and the ratio $b_s b_e/b^2$ does not exceed $\tfrac{1}{2}$. The main contribution in (9) comes from the first term. Its magnitude depends to a small degree on the type of dislocation, being $(1 - \nu)$ times higher for the screw one. This term differs by a negative factor from (7) and this means that, as the sample expands

in some direction by gliding, the small regions behind the moving dislocations are compressed in the same direction, regardless of the type of dislocation. This surprising result is the main outcome of our considerations. It enables us to determine the orientation of the centres.

The energy of a point defect in the elastic field is given by

$$E = -\mu \Omega_{ij} u_{ij} \tag{10}$$

where μ stands for the effective shear modulus of the medium, u_{ij} the deformation caused by an external stress σ_{ij} far from the defect, Ω_{ij} the dilatation tensor (for an interstitial-type defect $\Omega_{ll} = a^3$ where a is the size of the interstitial). As the centre is formed in the elastic field, E stands for the splitting of the energy barriers to produce the centre, so one may consider Ω_{ij} as the effective tensor of the barrier dilatation. We only consider the anisotropy of the effect, so, neglecting the terms in Ω_{ii},

$$E = -\tfrac{1}{2}\Omega_{ij}\sigma_{ij}. \tag{11}$$

For centres with C_3 or higher axes, one of the eigenvectors of Ω_{ij} coincides with the optical dipole direction d and with the symmetry axis. The special reference frame bound to the defect is used:

$$\Omega_{ij} = \begin{bmatrix} \Omega_1 & 0 & 0 \\ 0 & \Omega_1 & 0 \\ 0 & 0 & \Omega_3 \end{bmatrix} \tag{12a}$$

or, neglecting, as previously, the terms in Ω_{ii},

$$\Omega_{ij} = \Omega \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{12b}$$

With respect to the arbitrary frame of reference

$$\Omega_{ij} = d_i d_j \Omega \tag{13}$$

where the d_i stand for the components of d. The sign of Ω defines the effect of the elastic field on the centre orientation: Ω being negative, the centres 'prefer' the compression direction. Bringing together (5), (9), (10) and (13), we get

$$E(d) = [\mu\Omega b/2\pi(1 - \nu)R][(1 - \nu\, b_s^2/b)\, d \cdot t - \nu(b_s b_e/b^2)\, (d \cdot t)d \cdot (t \times n)] \tag{14}$$

for the orientation dependent part of the centre creation energy in the vicinity of the dislocation. Since only a very rough estimation of Ω and R is available, (14) only provides the order of the levels, the energy scaling factor remaining uncertain (about 20 meV for $\mu = 10^{11}$ Pa, $R/b = 5$, $\Omega = 1$ Å^3). For the sake of simplicity we introduce the orientation splitting parameter Δ:

$$\Delta = \Delta_1 + \Delta_2 \tag{15a}$$

$$\Delta_1 = (1 - \nu \cos^2\varphi)(d \cdot t)d \cdot n \tag{15b}$$

$$\Delta_2 = -\nu \sin\varphi \cos\varphi\,(d \cdot n)d \cdot (t \times n) \tag{15c}$$

where φ is the angle betwen the dislocation and its Burgers vector which is known for

Table 2. The splitting parameter Δ for the N_c centres in LiF ($\nu = -0.274$). (a) $\varphi = \pi/2, n = (011), t = (01\bar{1})$. (b) $\varphi = 0, n = (011), t = (01\bar{1})$.

d	Δ_1	Δ_2	Δ
(a)			
[010]	0.500	0.000	0.500
[100]	0.000	0.000	0.000
[001]	−0.500	0.000	−0.500
(b)			
[010]	0.637	0.000	0.637
[100]	0.000	0.000	0.000
[001]	−0.637	0.000	−0.637

Table 3. The splitting parameter Δ for the N–V centres in diamond ($\nu = -0.103$). (a) $\varphi = 0, n = (111), t = (1\bar{1}0)$, (b) $\varphi = \pi/5, n = (111), t = (1\bar{1}0)$, (c) $\varphi = \pi/3, n = (111), t = (1\bar{1}0)$.

d	Δ_1	Δ_2	Δ
(a)			
[1$\bar{1}$1]	0.300	0.000	0.300
[111]	0.000	0.000	0.000
[11$\bar{1}$]	0.000	0.000	0.000
[$\bar{1}$11]	−0.300	0.000	−0.300
(b)			
[1$\bar{1}$1]	0.292	0.017	0.310
[111]	0.000	0.000	0.000
[11$\bar{1}$]	0.000	0.000	0.000
[$\bar{1}$11]	−0.293	−0.017	−0.310
(c)			
[1$\bar{1}$1]	0.279	0.017	0.296
[111]	0.000	0.000	0.000
[11$\bar{1}$]	0.000	0.000	0.000
[$\bar{1}$11]	−0.279	−0.017	−0.296

dislocations in most of the crystals. Since ν is small, the dependence of Δ on φ cannot change the order of the levels. One can therefore predict the orientation of the centres no matter what dislocations move in the slip band. It boils down to tabulating the Δ values for all directions d possible for the given centre type. If Ω is known to be negative, the centres 'prefer' the orientation with maximum Δ.

The N_c band dichroism in the deformed LiF crystals disappears at lower temperature than is required for the dislocations to be annealed. The N_c absorption may be induced by the UV light; such action does not produce dislocations. The N_c centre is therefore a point defect in the host crystal rather than a dislocation trapped entity. Its orientation is influenced by the elastic (but not electric) field with a negative Ω value. The calculated model Δ parameter for LiF is given in table 2. It predicts the orientations of the [010] centres, which are confirmed by our measurements. According to the model, the centre orientation should not depend on the manner of loading since the dislocation field is much stronger than the external one. This was also the case in the experiment. If the N_c

centres are produced in a previously deformed sample they are not aligned. This is consistent with the model, since the conditions for the train hypothesis are not met. This leads us to believe that it is the dislocation train mechanism that controls the N_c dichroism in the plastically deformed LiF crystals.

Recently a small dichroism of about 500–600 nm in the plastically deformed diamond crystals was reported (Konstantinova *et al* 1988). Among the point defects in diamond (Davies and Hamer 1976) the trigonal N–V centre is the most appealing. It might be thought that it is formed by the dislocation when vacancies attach to the nitrogen impurities dispersed in the crystal. The Δ value calculated for the (111), [1$\bar{1}$0] slip system typical for diamond is given in table 3. For any dislocation either the [1$\bar{1}$1] or the [$\bar{1}$11] direction must be 'preferred' by the centre, depending on the sign of Ω. As the latter is unknown, we cannot make a choice between these two directions. Nevertheless this prediction might be checked experimentally; such a proof would be of great interest.

The proposed mechanism is therefore appropriate for dichroism in the deformed crystals. This does not mean that *any* type of dislocation moving in the crystal can produce the new centre—it depends on the microscopic nature of the process. But whenever the centre is created, it lies along the direction predicted by (15), since *all* dislocations have the train field as in (9).

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