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Comments on “Lattice Defects in Plastic Organic Solids”

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Comments on "Lattice Defects in Plastic Organic Solids"

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Hawthorne and Sherwood have recently published a series of papers on "Lattice Defects in Plastic Organic Solids", which constitute the first detailed investigations of the deformation behaviour of this type of compound.(1–3) These papers dealt with self-diffusion and plastic deformation during creep in pivalic acid, hexamethylethane, cyclohexane, succinonitrile and camphene. In this note we report some observations on the deformation behaviour of *dl*-camphor and succinonitrile which reinforce the conclusions of Hawthorne and Sherwood.

In plastic molecular crystals there is a transition temperature above which the molecules are able to rotate and the crystal structure changes to a higher symmetry, which is usually cubic.(4–6) These rotator phases are extremely soft and their entropies of fusion and dielectric constants indicate little configurational or rotational difference between the solid and liquid states.(4,7,8) This has led some workers to consider these compounds to be a distinct state of matter.(4,5) Hawthorne and Sherwood, however, have shown that the mechanism of creep in these crystals is similar to that found in other crystalline materials close to their melting points. They conclude that deformation during creep is diffusion controlled and probably occurs by a dislocation climb mechanism. In agreement with this, we find that the deformation behaviour of cubic rotator phases, rather than being unusual, is similar to that of other cubic materials.

Single crystals of zone-refined *dl*-camphor and succinonitrile were grown from the melt by the Bridgman method and also from the vapour under an atmosphere of nitrogen. Differential scanning calorimetry showed that for *dl*-camphor the transition to the rotator state occurred at 204.3 K with an enthalpy of transformation of 1.5 kJ mole^{-1}, and for succinonitrile at 232.8 K with an enthalpy of 8.7 kJ mole^{-1}. The rotator phases of both compounds have been reported to be f.c.c. although some doubt exists because of the difficulty of indexing the diffuse X-ray patterns obtained from compounds in which the molecules are rotating.(4,6,9,10) Calorimetry indicated that a second phase change occurred in *dl*-camphor at 350 K, with an associated enthalpy of 0.15 kJ mole^{-1}; the high temperature form appeared to be cubic when viewed under polarized

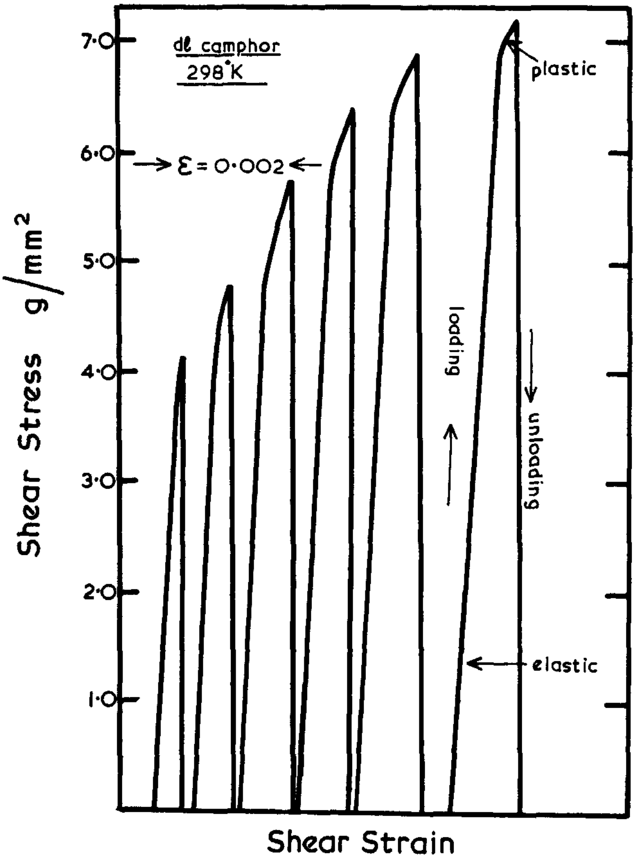


Figure 1. Shear stress-shear strain curve for *dl*-camphor single crystal deformed in tension at 298K at a strain rate of 0.002 per minute showing the effect of repeated loading and unloading.

light whereas the low temperature form was not cubic. It is thought that *dl*-camphor has a f.c.c. structure above 350 K and a heavily faulted f.c.c. structure between 350 and 204.3 K.

Single crystal rods of *dl*-camphor and succinonitrile, 10 mm long and 3.5 mm diameter, were deformed in uniaxial tension, compression or shear at 298 K in an Instron tensile machine at strain rates from 0.002 to 0.100 per minute. Under all deformation conditions, stress-strain curves were obtained which showed a marked elastic region prior to the onset of plastic deformation at stresses of 4–5 g/mm^2 for *dl*-camphor and 2–3 g/mm^2 for succinonitrile (Fig. 1). Cycling of the load on a crystal gave stress-strain curves which were identical, except for the increased yield stress due to work-hardening (Fig. 1). This behaviour is typical of a material which deforms by crystallographic slip. Analysis of slip traces on the surface of deformed single crystals indicated that deformation occurred, as in other f.c.c. materials, on the $\{111\}$ planes in the $\langle 110 \rangle$ directions. This is illustrated in Fig. 2 which shows slip traces in the (111) surface of a vapour-grown camphor crystal due to slip on the other three $\{111\}$ planes after indentation of the surface using a Leitz micro-hardness tester.

Deformed single crystals of *dl*-camphor and succinonitrile recrystallise readily at room temperature to form polycrystalline specimens; the kinetics of recrystallisation and grain growth are similar to those of metals at comparable fractions of the absolute melting point. The yield stress of polycrystalline camphor depends on the grain size and, in marked contrast to single crystals, the rate of work-hardening is low (10–20 compared with 700–800 g/mm^2/100 pct strain). This is probably due to the extensive grain boundary sliding which occurs on deforming polycrystalline camphor.

Crystallographic slip is not the only mechanism of deformation in these rotator phases. Mechanical twinning of *dl*-camphor at 298 K can be induced by rapid loading of single crystal rods parallel to their axis or by rapid identation of the (111) surface of vapour grown crystals (Fig. 3). Analysis of traces in different surfaces showed that the twinning system was $\{111\}$ $\langle 112 \rangle$, as in f.c.c. metals. The ease of twinning in *dl*-camphor is indicative of a comparatively low stacking fault energy as f.c.c. metals usually do not form mechanical twins except at low temperatures under shock-loading conditions.

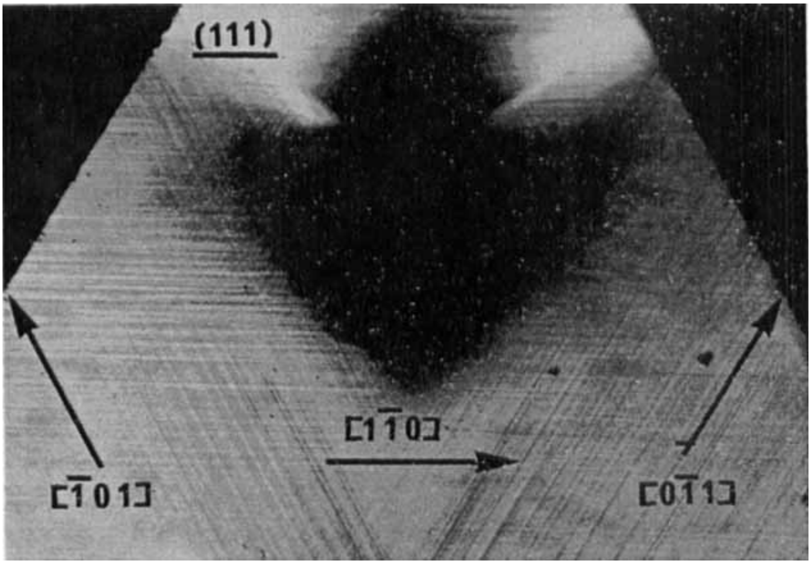
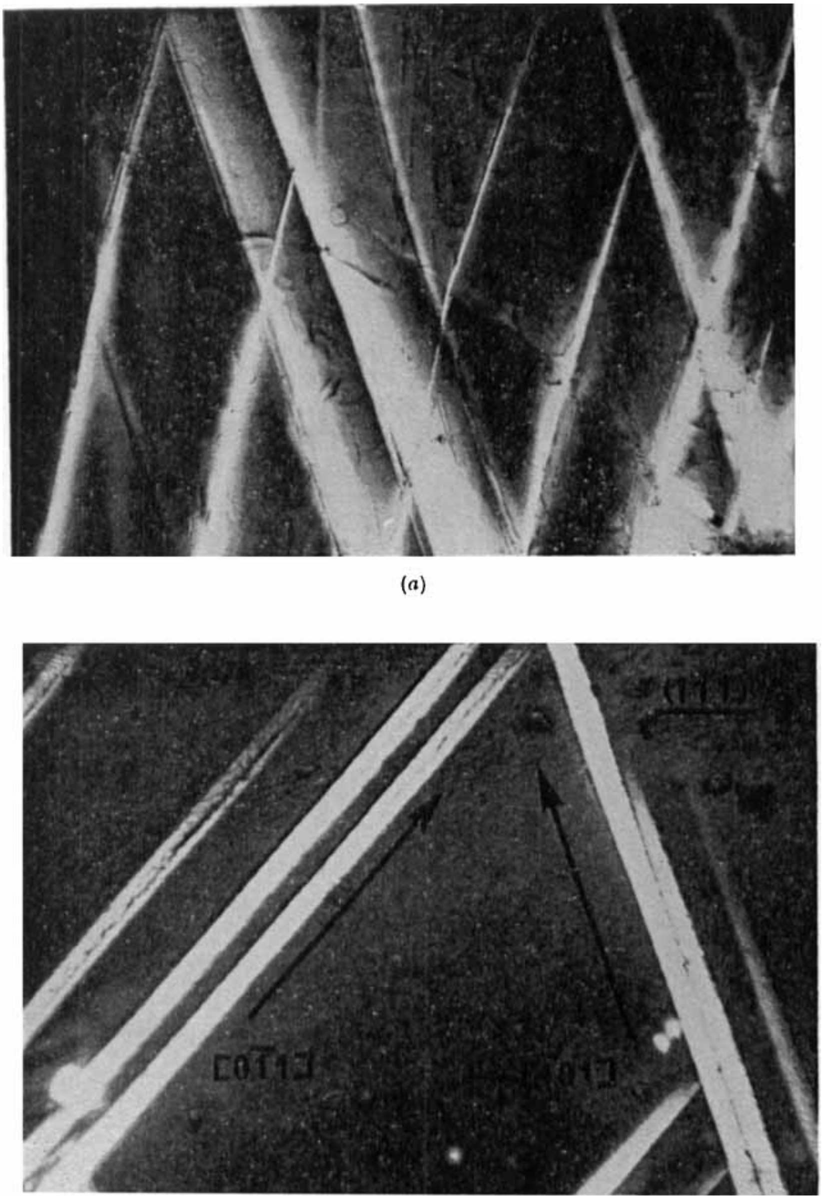


Figure 2. Slip traces at 60° to one another in the (111) surface of a vapour-grown *dl*-camphor single crystal due to slip on three of the {111} planes after identation using a Leitz micro-hardness tester. Obliquely incident reflected light, × 360.

The ready formation of twins is consistent with a heavily faulted f.c.c. structure between 204.3 and 350 K.

The results outlined above give more direct evidence than the creep experiments of Hawthorne and Sherwood that plastic molecular crystals are similar to other materials as far as their deformation behaviour is concerned. Thus, although the rotator phase of *dl*-camphor and succinonitrile appear to be soft and waxy, deformation occurs either by slip or twinning on the same crystallographic systems as other f.c.c. materials. The extreme softness is a consequence of the very weak intermolecular forces in these materials, combined with a high crystal symmetry leading to a proliferation of favourable crystallographic slip systems.



(a)

(b)

Figure 3. Deformation twins in (*a*) a single crystal rod of *dl*-camphor rapidly loaded parallel to the rod axis and (*b*) the (111) surface of a vapour-grown single crystal after rapid identation. Polarised transmitted light, × 100.

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