The breakaway process seems to have started from a high driving force region at the lower right corner. The old grooves are seen to have been left behind while the new grooves are following the boundaries.

For most of the frames in Fig. 2 the shape of the shrinking grain remains similar, as shown in Fig. 3 by the measurements of the angles and the lengths of the four grain-boundary arcs as a function of time. However, the situation seems to change at the 18th frame. One of the boundaries starts to become straight and the angle decreases toward zero. Other boundaries seem to experience similar changes until the whole grain disappears.

Since the boundaries cannot move without the junctions moving at the same time and vice versa, the slow moving ones are rate controlling. When the driving force is small, the boundaries move slowly and the junctions seem to have plenty of time to follow the boundaries and adjust themselves to nearly equilibrium configurations. This is the situation for most of the frames in Fig. 2. The motion of the boundary is the rate controlling process. However, when the boundary velocity is sufficiently high so that the junctions cannot follow easily, the local equilibrium at the junctions is upset and the angles of the boundary arcs begin to change. Finally, the boundary velocity is limited by the junction velocity. When that happens, the boundaries have sufficient mobility to follow the junctions and to adjust themselves to nearly equilibrium configurations, namely planar (or straight in the picture) boundaries. The junction motion is then the rate controlling process. Details will be published soon.

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Factors determining the electric strength of polymeric dielectrics

The problem of the electric strength of solid dielectrics has been tackled by many investigators, and different theories have been put forward to explain the phenomena of electrical breakdown [1].

The effect of intermolecular forces on alkali halide crystals has been shown by Vorob'ev [2], who established a correlation between the different physical properties of alkali halides (such as hardness, compressibility, melting point and electric strength) and the lattice energy. A linear relationship has more recently been found by Vijh [3–5] between related molecular parameters (lattice space and energy), the electric strength, and the elastic moduli of the alkali halides. This leads to the conclusion that the factors determining the thermal, mechanical and electrical properties are synonymous.

It has been suggested by Artbauer [6, 7] that there is a considerable significance of the molecular structure on the electric strength of polymeric materials. The important factors are the intermolecular forces acting between the different macromolecules (secondary bonding) and the free volume presented in all polymers. Artbauer [7] concluded that the time and temperature dependence of the electric strength is mainly due to molecular relaxation processes.

The effect of molecular motion due to electric stress has been studied in this laboratory by means of the photo-elastic technique. Test specimens fabricated from epoxy-resins (CIBA CT200 + Hardener HT901) were moulded around two stainless steel conic electrodes having a tip radius of 2 mm. and maintained at a distance of 100 to 200 μm. Paraffin oil was used to suppress unwanted disch-

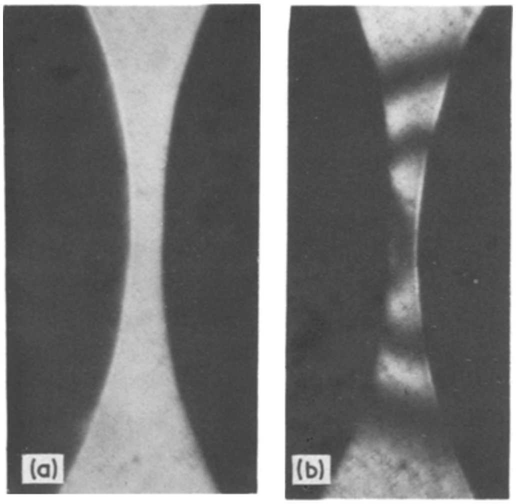

Figure 1 (a) Specimen supporting a voltage of 50 kV at 103° C. Gap distance 150 μm. (b) Specimen after stressing with 30 kV at 105° C and cooled to 103° C (photograph taken after removal of the electric stress).

arges and to act as a heating medium. Specimens with 20% hardener did not display any deformation when subjected to a direct stress of 50 kV normal to the polarized beam, at temperatures up to 104° C (Fig. 1a). Signs of deformation at a much lower voltage, however, were observed beyond 105° C. These deformation fringes vanish as soon as the voltage is reduced to zero. However, it was possible to freeze the fringes by cooling the specimen rapidly to 103° C whilst maintaining the electric stress. These fringes are visible (Fig. 1b) even after the removal of the stress. It is no coincidence that 105° C is the glass transition temperature for this material and different critical temperatures could be obtained for different hardener ratios [8]. They are similar to the results of Baud and Racké [9], who used a purely mechanical load for the determination of the glass transition temperature of different epoxy-resin compositions.

In order to compare the electric strength of different polymers with their intermolecular forces, it is necessary to do so at very low temperatures, so as to avoid the transition phenomena occurring in the structure. The electric strengths will then have their characteristic values [1]. The lowest measured glass transition for polymers is that for silicon rubber with $T_g = -123°$ C. As a result, the values at liquid nitrogen temperature should be sufficient for comparison.

The cohesive energy density (CED) is a parameter which characterizes the energy required to separate the closed structure into infinitely separated molecules [10].

$$\text{CED} = \delta^2 = E_{\text{vap}}/V_{\text{m}}$$

where δ is the solubility parameter, E_{vap} the evaporation energy, and V_{m} the molar volume.

A comparison between the cohesive energy density and the electric strength of different polymers is given in Table I. It is evident that polar materials having a high CED yield the highest electric strengths. Furthermore, such materials may also be identified by their change in strength, which is a continuously decreasing function of temperature due to the break up of dipole-dipole interactions. This contrasts with non-polar materials having a more constant strength in the glassy state.

The foregoing give some encouragement that ideas developed for the electrical breakdown of ionic crystalline materials may be extended, with certain restrictions, to explain the electrical properties exhibited by amorphous or partially crystalline polymers.

TABLE I Comparison of the electric strength of some polymeric materials with their cohesive energy densities (CED)

Polymer		δ	CED (cal cm^{-3})	E_d(MV cm^{-1}) at. −195° C
Polydimethylsiloxane	Non-polar	7.3	53.3	2.1 [6]
Polyisobutylene		7.8	60.8	5.1 [14]
Polyethylene		7.9	62.4	6.8 [13]
Polybutadiene		8.1	65.6	6.5 [8]
Polystyrene		9.1	82.8	7.2 [14]
Polyvinylacetate	Polar	9.4	88.4	12.2 [13]
Polymethylmethacrylate		9.5	90.2	13.4 [14]

Data for δ are from references 10, 11 and 12.

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The cohesion of the metals of group IB

It appears to be generally agreed that the cohesion of group IB elements is much greater than would be expected for univalent metals: equally it is not clear as to why this should be so, as commentaries on the topic [1, 2] indicate. The basic difficulty lies in finding an acceptable postulate regarding an additional contribution to the cohesion from underlying electrons. In a recent paper [3], in which, *inter alia,* the constitution of some compounds of transition metals with B-group elements was discussed, it was hypothesized that a strong ionic contribution existed for example in the bonding of NiAl, and, by inference, in analogous compounds such as beta-brass CuZn; in effect, for the latter we may write $Cu^{2-}Zn^{2+}$, although the situation is better expressed in Fig. 1, which schematically shows ionic combination of zinc valency electrons into the d-shell of copper with simultaneous release of electrons from the copper. Now if this explanation is valid, there would seem to be no *prima facie* reason why the same type of process may not operate in metallic copper, as illustrated in Fig. 2. It is perhaps easier to picture the latter as a resonance or consecutive reaction (as drawn in Fig. 2, cf. Fig. 1 and [4]) because of the identity of atomic species, and this interpretation is probably consistent with the evidently lower mechanical strength in copper compared with beta-brass [5, 6] and with the 0.5 T_m type (i.e. a metallic type) of oxidation classification [7] for copper again contrasted with beta brass [8], although it may not be so satisfactory with respect to the transport properties. The hypothesis is attractive; however, further work will be necessary to establish if it is compatible with the broader sequence of changes in bond mechanisms as we proceed along the periods of the Table, and whether or not it may be extended to neighbouring groups VIIIC and IIB. A well-known text [9] touches upon many points of interest related to the present purpose, although the standpoint is essentially different.

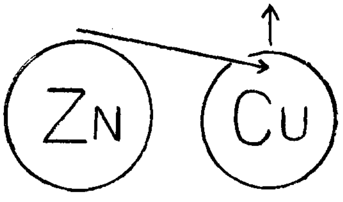

Figure 1.

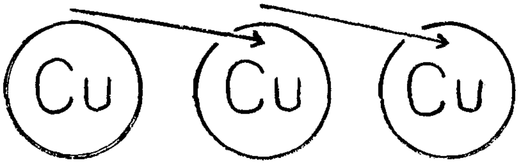

Figure 2.

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