within the bond-orbital model the nearest neighbour bonding matrix element has a d^{-2} dependence on bond length. This relation was also found to hold for other nearest-neighbour matrix elements [5], and Pantelides [6] has extended these ideas to show that

$$E_{\mathbf{g}} = N_{\mathbf{g}} \left(\hbar^2 d^{-2} / m \right) \tag{2}$$

where $N_{\rm g}$ is a dimensionless constant called the band-gap index. For the alkali halides it was shown that $N_{\rm g} = 9.1$. $N_{\rm g}$ is a function only of the chemical valence of the constituent atoms and obeys the empirical relation

$$N_{\rm g} = N_{\rm go} - 3.8Z \tag{3}$$

where N_{go} is the band gap index of the rare gas solids, 12.9, and Z the valence [6]. Pantelides [6] has shown that Equation 2 is obeyed for a wide range of materials—rare gas solids, alkali halides, chalcogenides, and pnictides. Thus, on the basis of Equations 1 and 2, it is readily seen that a relation

$$F = Ba^{-6} \tag{4}$$

exists where $B = 1.7 \times 10^{-3} (N'_{g}h^{2}/m)^{3}$ and N'_{g} is a new band-gap index which accounts for the relation between bond length and lattice constant for these solids. It can be seen that Equation 4 is qualitatively consistent with Vijh's correlation.

It was previously mentioned that Vijh rationalized the correlation between F and a by considerations of solid state cohesion. Figure 1 also shows a plot of F versus cohesive energy, indicating that

Fracture mode transitions in polymethylmethacrylate

A recent paper [1] described measurements on the fracture behaviour of polymethylmethacrylate (PMMA) in the crack-speed range 10^{-3} to 10^{0} m sec⁻¹, and discussed the transition from slow stable crack propagation to fast unstable crack propagation that occurs in PMMA, at room temperature, at approximately 2×10^{-2} m sec⁻¹. Various explanations of this transition were referred to, including a change in the mode of formation of crazes ahead of the crack tip from one plane at low velocities, to a multiplane mode at higher velocities [2]. This fracture mode change was described in [2] to explain the transition between the macroscopically

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such an approach is reasonable. However, we feel that our approach is certainly physically meaningful when one considers the physical phenomena occurring at dielectric breakdown, i.e. the width of the energy gap is the pertinent parameter. For a complete review of dielectric breakdown in solids, see the article by O'Dwyer [7].

References

- 1. A. K. VIJH, J. Mater. Sci. 9 (1974) 2052.
- 2. Idem, ibid 5 (1970) 379.
- 3. W. A. HARRISON, Phys. Rev. B 8 (1973) 4487.
- 4. W. A. HARRISON and S. CIRACI, *ibid* 10 (1974) 1516.
- 5. S. T. PANTELIDES and W. A. HARRISON, *ibid* 11 (1975) 3006.
- 6. S. T. PANTELIDES, ibid 11 (1975) 5082.
- 7. J. J. O'DWYER, Adv. Phys. 7 (1958) 349.
- D. E. GRAY, Ed., "American Institute of Physics Handbook" (McGraw-Hill, New York 1972) pp. 9-17.
- 9. C. KITTEL, "Introduction to Solid State Physics", 4th Edn. (Wiley, New York, 1971) p.121.

Received 1 September and accepted 18 September 1975

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smooth surface and the striated macroscopically rough surface that occurs in PMMA in the fracture velocity range 400 to $500 \,\mathrm{m \, sec^{-1}}$. Consequently, the comment in [1] that the multiplane crazing explanation was inconsistent with observed features on the lower speed stable/unstable fracture transition is hardly surprising.

A further effect was suggested in [2], that the stable/unstable fracture transition at low speeds is a change from the process of formation of a single, coherent well-defined craze ahead of the crack, and its subsequent splitting, at low crack speeds; to the formation of numbers of crazes ahead of the crack tip and their subsequent coalescence at higher speeds. Below crack speeds of approximately 400 m sec⁻¹, these crazes are formed substantially on

the same plane, that of the crack front.

This is not suggested as alternative to the description of an isothermal/adiabatic transition in fracture behaviour [3], but as a corollary. One can consider the mechanisms in [3] as happening at the molecular level and that in [2] as a phenomenon on the microscopic level, or they can equally well be regarded as cause and effect of the low speed fracture transition in PMMA. This explanation of the stable/unstable fracture transition appears to be consistent with the data in [1] especially when one compares the appearances of the fracture surfaces obtained in these investigations [2, 4, 5], which are strikingly similar.

References

- 1. A. G. ATKINS, C. S. LEE and R. M. CADDELL, J. Mater. Sci 10 (1975) 1381.
- A. K. GREEN and P. L. PRATT, Eng. Fract. Mech. 6 (1974) 71.
- 3. J. G. WILLIAMS, Int. J. Fracture Mech. 8 (1972) 393.
- 4. A. G. ATKINS, C. S. LEE and R. M. CADDELL, J. Mater. Sci 10 (1975) 1394.
- 5. A. K. GREEN, Ph.D. Thesis, London University (1971).

Received 12 September and accepted 29 September 1975

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Some studies on the thermal solid state stability of zircon

It is known that the mineral zircon $(ZrSiO_4)$ can thermally dissociate to form zirconia (ZrO_2) and either an amorphous form of silica (SiO_2) or a highly siliceous liquid depending on the temperature. However, there is no general agreement as to the temperature at which solid state dissociation begins.

Using X-ray diffraction, Curtis and Sowman [1] carried out a series of investigations on zircon

samples of high purity (\pm 99%), including dissociation kinetics, reassociation of dissociated zircon, synthesis of zircon from zirconia and various allotropic forms of silica, and on some phase relations in the system ZrO_2 -SiO₂. From their experimental conclusions they drew the equilibbrium phase diagram of ZrO_2 -SiO₂ system presented in Fig. 1. For Curtis and Sowman the domain of the solid state dissociation of zircon is contained between ~ 1540 and ~ 1677° C, 1540° C appearing to be the highest temperature at which zirconia and silica combine to yield zircon and the



Figure 1 Equilibrium phase diagram of the ZrO₂-SiO₂ system proposed by Curtis and Sowman [1].
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