

THE PRESSURE DEPENDENCE OF THE OPTICAL GAP IN CRYSTALLINE
AND AMORPHOUS ARSENIC TRISELENIDE

A.J. Grant and A.D. Yoffe

Surface Physics, Cavendish Laboratory, Cambridge, England

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The effect of hydrostatic pressure on the optical absorption edge of crystalline and amorphous samples of arsenic triselenide As_2Se_3 has been measured at 80°K and 274°K, at high values of optical absorption coefficient (10^3 – 10^4 cm^{-1}). The contributions of the electron-phonon interaction and of the lattice dilatation to the total temperature shift of the optical absorption edge in amorphous As_2Se_3 have been evaluated.

THE RECENT observation of electrical switching in devices which employ chalcogenide-based glasses as the active element has stimulated great interest in the properties of disordered solids. Arsenic triselenide As_2Se_3 may be prepared both as a layer crystal and in the amorphous form, and it is therefore a particularly appropriate system for comparative studies of the effect of disorder on the electronic properties.

The optical absorption spectra of crystalline and amorphous As_2Se_3 have been measured previously in this laboratory.¹ This paper describes the effect of hydrostatic pressure on the optical absorption edge in crystalline and amorphous As_2Se_3 at high values of the optical absorption coefficient, between 10^3 and 10^4 cm^{-1} . We consider it essential to measure pressure and temperature coefficients at high values of optical absorption coefficient if the values are to be attributed to the associated direct optical band-gap. This procedure greatly reduces the likelihood that the pressure or temperature shift will be obscured by the accompanying broadening of the optical absorption edge. At low values of optical absorption coefficient it is even possible that the wrong sign of a temperature or pressure coefficient may be obtained if care is not taken with respect to broadening.

The pressure dependence of the photo-conductivity spectra of crystalline and amorphous As_2Se_3 has recently been reported² and the results are in qualitative agreement with the present work.

Hydrostatic pressures up to 5 kbar were used with helium gas as the pressure fluid. The sample cell could be cooled to liquid nitrogen temperature. The crystals of As_2Se_3 were grown in this laboratory by vapour phase sublimation from the powder of 5N purity. The crystals were cleaved to a thickness of one or two microns and were mounted on the sapphire window of the high pressure optical cell. The amorphous films of As_2Se_3 were prepared by evaporation on to Spectrosil substrates.

Crystalline and amorphous samples of As_2Se_3 each exhibited a parallel shift of the optical absorption edge to lower energy under pressure. The pressure shifts were linear and reversible within the experimental accuracy, and the resulting pressure coefficients are given in Table 1. The average temperature coefficients of the optical absorption edge at the same high values of optical absorption coefficient were estimated from the spectra of reference 1. Unpolarised light was used in this work.