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

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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.

Table 1. The pressure and temperature coefficients of the optical absorption edge in crystalline and amorphous As_2Se_3

As_2Se_3	T ($^\circ\text{K}$)	Energy E (eV)	$(\partial E/\partial P)_T$ $\times 10^{-6}$ eV/bar	$(\partial E/\partial T)_P$ average $\times 10^{-4}$ eV/deg.
crystal	274	2.0	-14.0 ± 1.0	
	80	2.1	-10.0 ± 0.8	-7.9
amorphous film	274	1.98	-7.6 ± 1.5	
	80	2.10	-11.5 ± 1.0	-5.6

The pressure coefficients for crystalline and amorphous samples of As_2Se_3 at 80°K are very similar, which indicates that the presence of long range order is not a critical factor. The pressure coefficient for crystalline As_2Se_3 increases with increasing temperature, which is 'normal' behaviour much like that observed in other crystalline materials. Amorphous As_2Se_3 however behaves in an unusual manner, having a pressure coefficient of the optical absorption edge which is considerably smaller at 274°K than at 80°K .

Thermal expansion coefficients for arsenic-selenium glasses have been measured,³ and for the composition As_2Se_3 , the linear thermal expansion coefficient has the value 2.0×10^{-5} /deg. at room temperature. The compressibility² of amorphous As_2Se_3 has the value 1×10^{-5} cm²/kg, or 1.02×10^{-5} /bar.

The temperature and pressure coefficients of the optical energy gap are related as follows

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\alpha}{\beta} \left(\frac{\partial E}{\partial P}\right)_T$$

where α is the volume thermal expansion coefficient and β is the isothermal bulk compressibility. The first term on the right hand side gives a measure of the electron-phonon interaction, and the second term represents the contribution of lattice dilation to the total temperature shift, expressed in terms of α , β and the pressure coefficient.

In the case of amorphous As_2Se_3 at room temperature, the lattice dilation term has the value 0.45×10^{-4} eV/deg., whereas the total eV

temperature coefficient is much larger, -5.6×10^{-4} eV/deg. The electron-phonon term thus has the value -6.0×10^{-4} eV/deg., and dominates the total temperature coefficient. No values for α and β for crystalline As_2Se_3 appear to have been published, but from the pressure and temperature coefficients in Table 1 it is clear that the electron-phonon term will again be very large and negative. Further studies are planned to investigate the mechanism of the electron-phonon interaction, which appears to be considerably stronger in As_2Se_3 than in the more familiar semiconductors such as silicon and germanium,⁴ and also in layer type solids which are truly two-dimensional such as the transition metal dichalcogenides.⁵

There is a certain structural similarity between As_2Se_3 and trigonal selenium Se, since both have long spiral chains of atoms, and the similarity may extend to the electronic properties of both materials. The temperature^{6,7} and pressure^{8,9} coefficients of the optical gap in Se are closely similar in magnitude and sign to those for As_2Se_3 , which implies that Se will also have a large negative electron-photon interaction term. In addition, the pressure and temperature dependence of the optical absorption edge (at low values of optical absorption coefficient, $< 10^2$ cm⁻¹) in a glass used for switching devices, $\text{Ge}_{16}\text{As}_{35}\text{Te}_{28}\text{S}_{21}$ has been measured.¹⁰ The pressure and temperature coefficients are both negative, and the lattice dilation is again found to provide the minor contribution to the total temperature coefficient. The large negative electron-phonon term is therefore a property which is common to crystalline and amorphous As_2Se_3 , trigonal Se, and a chalcogenide-based glass. A possible explanation for the large

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negative explicit temperature coefficient
($\partial E/\partial T$)_V in terms of the large increase in the
volume of the As₂Se₃ chains with temperature
relative to the overall volume of the crystal is
given by Mott.¹¹

The large negative pressure coefficients of
the optical gap in crystalline and amorphous
As₂Se₃ gives reason to expect contributions to

the valence levels involved in the optical
transitions from electrons of s-like symmetry
derived from As or Se 4s atomic states. An
alternative argument could relate to the
anisotropy of this material independent of the
symmetry of the bands. Band structure
calculations which are at present under way
will be of value in determining the energy
levels which give rise to the optical absorp-
tion edge.

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On a regardé l'effet d'une pression hydrostatique sur le spectre d'absorption optique d'échantillons cristallins ou amorphes de As₂Se₃ à 80°K et 274°K dans la limite de forts coefficients d'absorption optique (de 10³ à 10⁴ cm⁻¹). Dans le cas de As₂Se₃ amorphe, on a évalué les contributions dépendant de la température au spectre d'absorption optique provenant de l'interaction électron-phonon ou de la dilatation du réseau.