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

As_2Se_3	T (°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	-5.6
	80	2.10	-11.5 ± 1.0	

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 compressibility[2] of amorphous As_2Se_3 has the value 1×10^{-5} cm^2/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, $Ge_{16}As_{35}Te_{28}S_{21}$ 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