F I Z I K A V O L U M E 10 S U P P L E M E N T 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics of Condensed Matter, Kruševac, September, 18-22, 1978

SOME OPTICAL PROPERTIES OF GERMANIUM DICHALCOGENIDES

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ABSTRACT

Infrared room temperature reflectivity spectra have been measured with polarised light for single crystals of GeS_2 and $GeSe_2$ in the range 40-600 cm^{-1} for $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ directions. Optical parameters were calculated using both Kramers-Krönig integration and a fitting procedure. A comparison of the phonon frequencies of the corresponding Raman and infrared modes in the spectra of GeS_2 and $GeSe_2$ were made and intercrystal frequency ratio were detrmined $C_0=\nu_i(GeSe_2)/\nu_i(GeS_2)=0.68$.

1. INTRODUCTION

GeS_2 and $GeSe_2$ crystallise as layered crystals in which the molecular unit is infinitely extended in two dimensions. In both compounds the germanium atoms are sendwiched between two layers of sulphur or selenium atoms so that the unit of three layers is periodically repeated in the pattern X-Ge-X - X-Ge-X; X=S or Se. In each layer the Ge and S or Se atoms are connected by strong intralayer covalent forces, while the interlayer forces are of the weak Van der Waals type.

Germanium dichalcogenides crystallise in an orthorhombic system, and both have a symmetry described by the D_{2h}^{13} space group[1]. The unit cell contains 24 atoms. Besides this there are also some other crystal modifications: monoclinic[2], tetragonal (GeS_2)[3] and orthorhombic $GeSe_2$ with 16 atoms per unit cell[4].

This paper reports an experimental investigation of the lattice vibrations of crystalline GeS_2 and $GeSe_2$. The phonon spectra have been studied in far-infrared reflectivity measurements (reststrahlen), and in Raman-scattering experiments[5]. Experimental results were analysed using both Kramers-Krönig integration and a fitting procedure.

2. EXPERIMENTAL

Single crystal of GeS_2 and $GeSe_2$ were made using a standard Bridgemann technique. Details of the crystal growth have already been published elsewhere[6].

Polarised infrared reflectivity spectra of GeS_2 and $GeSe_2$ were measured on oriented single crystals at room temperature. The measurements on planes perpendicular to the $\vec{c}$-axis were made with freshly cleaved surfaces. For measurements with light parallel to the $\vec{c}$-axis the samples were cut and polished perpendicular to the cleavage planes.

The infrared reflectivity spectra were measured on a Beckmann FS 720 Fourier spectrometer in the frequency range 20-400 cm^{-1} and on a Perkin-Elmer type 577 spectrophotometer in the range 200-4000 cm^{-1}.

Raman spectra were taken at room temperature with back-scattering geometry using an Ar^+ laser.

3. RESULTS AND DISCUSSION

The near-normal-incidence far-infrared reflectivity spectra of single crystals of GeS_2 and $GeSe_2$ for $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ polarisation are shown in fig.1. The points, in fig.1, are oscillator analysis theoretical fits; the solid lines are experimental results.

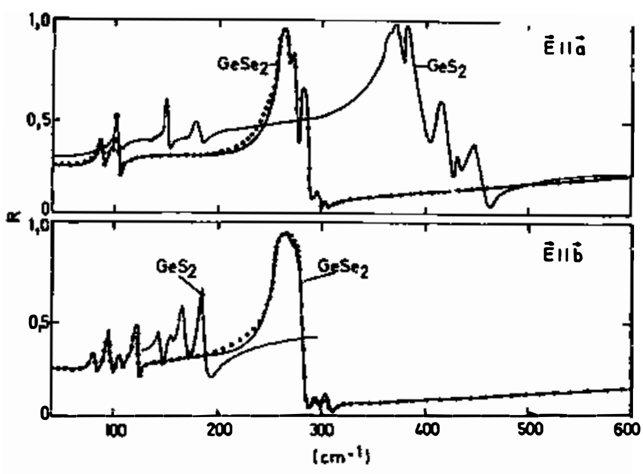

Fig.1. Experimental far-infrared reflectivity data (solid lines). The points were oscillator-analysis theoretical fits with parameters given in Table 1.

Reflectivity spectra for GeS_2 were numerically analysed using the Kramers-Krönig integration method and reststrahlen spectra for $GeSe_2$ with a fitting procedure using a four-parameter model. The values of the optical parameters obtained with the fitting procedure and Kramers-Krönig integration method are given in Table 1.

TABLE 1. Oscillator parameters for GeS_2 and $GeSe_2$.

	GeS_2				$GeSe_2$			
	ω_{jTO}	ω_{jLO}	ε_0	ε_∞	ω_{jTO}	ω_{jLO}	ε_0	ε_∞
	100	102			88	89.5		
	150	152			99	100		
	178	182			103	105		
$\vec{E}\parallel\vec{a}$	366	376	9.5	7	262	272	10	7
	382	392			269	277		
	410	419			281	291		
	430	432			297	298		
	442	456			303	305		
	142	145			82	83		
	152	154			96	98		
	164	169			104	107		
$\vec{E}\parallel\vec{b}$	183	188	11.5	8	123	124.5		
					261	288		
					292.5	298		
					304	306		

Germanium dichalcogenides have rather interesting reflectivity spectra. No inorganic semiconductor shows similar behavior. There is a large number of oscillators for both compounds which is what one would expect for a structure with 24 atoms per unit cell, and low symmetry of space group D_{2h}^{13}. In interpreting the observed spectra it is essential to analyse group theoretically the diperiodic layer symmetry. Since, GeX_2(X=S,Se) space group literature data are in disagreement (C_{2v}^{19} by Wyckoff[7]) and D_{2h}^{13} by Cjun-Hua[1])) and the atom positions in the unit cell are not known, it is not possible to find out the number of either Raman or infrared active modes.

There is an obvious analogy between the germanium dichalcogenide spectra given in fig.1. Because the crystal structure and the symmetry of both GeS_2 and $GeSe_2$ are the same, one should not expect any differencies in the shape of their reflectivity spectra. It was only noticed that the position of reststrahlen peaks was moved towards the smaller frequencies, when lighter S atoms are changed with heavier Se atoms.

It is interesting to notice that for $\vec{E}||\vec{c}$ polarisation with both compounds there was an oscillator in the range between 331 and 340 cm^{-1}. The origin of this oscillator might be in the vibration of the Ge-Ge pair of atoms, because this oscillator was also observed for pure Ge[5]..

In figure 2 the frequencies of Raman and infrared active-zone-center phonons in $GeSe_2$ are plotted agains the corresponding phonon frequencies in GeS_2. The Raman spectrum was made with non-polarised light[5,8] and IR spectrum with light polarised in $\vec{E}||\vec{a}$ and $\vec{E}||\vec{b}$ directions[5]. Each point in the figure specifies the pair of frequencies, $\nu_i(GeSe_2)$ and $\nu_i(GeS_2)$, which belong to the same eigen vibration (presumed the same, or very similar, via the spectral correspondence) in the two closely related crystals. The solid lines passing through the data for low and high frequencies are obtained using a linear fit, by the least squares[9] method. The ratio of the phonon frequencies of corresponding modes of $GeSe_2$ and GeS_2 is $C_0=0.68\pm0.02(\nu(GeSe_2)=C_0\nu(GeS_2))$. Since, $C_0=C_\mu C_k$[9], where is $C_k=[k_0(GeSe_2)/k_0(GeS_2)]^{1/2}$ and $C_\mu=[\mu_0(GeSe_2)/\mu_0(GeS_2)]^{-1/2}$ (k_0 is the Ge-X bond stretching force constant and μ_0 is reduced mass) and C_μ for Ge-dichalcogenides is 0.72, it follows that $C_k^2=(C_0/C_\mu)^2\approx0.90$. The results indicate that intralayer bonds in $GeSe_2$ are about 10% softer than those in GeS_2.

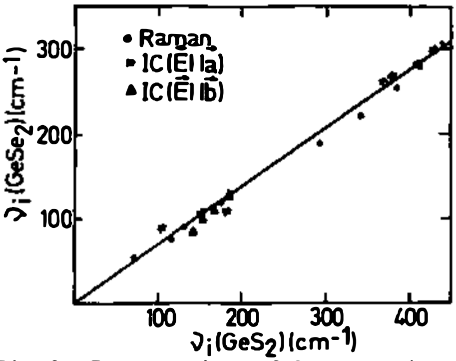

Fig.2. Frequencies of Raman and infrared-active zone-center phonons in $GeSe_2$ plotted against the corresponding phonon frequencies in GeS_2. The solid lines are the results of a linear least squares fit through the data points.

Complete analysis of the lattice vibrations of either $GeSe_2$ or GeS_2 will be possible when the factor group analysis is done. This work is in progress.

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