

THE LATTICE VIBRATION OF SOME LAYERED IV-VI SEMICONDUCTORS

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The germanium and tin chalcogenide compounds: GeS, SnS, GeSe and SnSe can be considered as essentially two dimensional semiconductors. They have a sandwich structure X-M-M-X with a very weak interaction between the layers and crystallize in an orthorhombic B29 structure with a D_{2h}^{16} space group. Recently several papers have been published discussing the effects of interlayer forces on the infra red and Raman active phonon frequencies, mainly of GeS (1,2).

In this work far infra red reflectivity measurements are reported for single crystals of GeS and SnSe these have been analysed using the Kramers-Krönig integration procedure.

We have prepared single crystal specimens of these four semiconductors by the Bridgmann technique. The crystals are easily cleaved in a direction perpendicular to the c - axis.

The details of this preparation have been given elsewhere (3). Far infra red reflectivity measurements for polarized light were made in the frequency range between $40-400 \text{ cm}^{-1}$ using Beckmann Fourier spectrophotometer FS 720. These measurements have been done at room and liquid nitrogen temperatures.

Figure 1. shows some typical reflectivity results for the GeS sample at 77 K for light polarized $\vec{K} \parallel \vec{a}$. In this case three peaks corresponding to three ionic resonances were observed, although Wiley 1 observed only two resonances at room temperature. In figure 2 similar room tempe-

perature reflectivity diagrams are given for SnSe for the polarization $\vec{K} \parallel \vec{a}$ and $\vec{K} \parallel \vec{c}$.

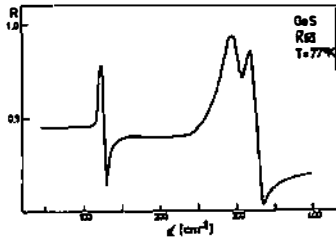


Fig. 1

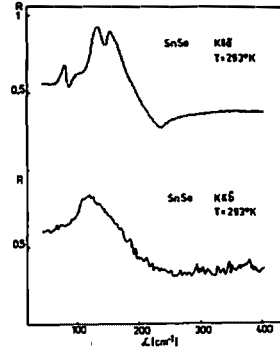


Fig. 2

The reflectivity data for these and the other layered semiconductors were analysed by Kramers-Krönig techniques and the results of these analyses are given in Figure 3 and table 1. Figure 3 shows diagrams for the real (ϵ') and imaginary part of the dielectric constant (ϵ'') for SnSe. Table 1 displays phonon frequencies in units of cm^{-1}

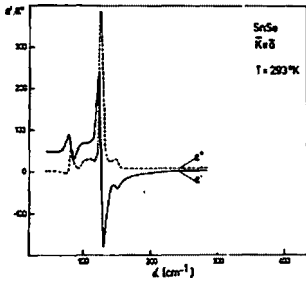


Fig. 3

(ω_{TO} and ω_{LO} are transversal and longitudinal optical modes respectively). In the case of tin chalcogenide ω_{TO} lie between the two corresponding values for the germanium chalcogenides. Raman studies of all

these compounds are necessary to determine the ratios of the variations intralayer to interlayer force constants. As far as we know these data are

TABLE I

	TO_1	LO_1	TO_2	LO_2	TO_3	LO_3	ϵ_0	ϵ_∞
GeS $\vec{K} \parallel \vec{a}$ (77K)	122	124	283		307	329	25	6
SnS $\vec{K} \parallel \vec{a}$	97	105	180	215	217	285		
SnS $\vec{K} \parallel \vec{b}$	192	290						
SnSe $\vec{K} \parallel \vec{a}$	80	88	126	129	146	218	48	2.5
GeSe $\vec{K} \parallel \vec{a}$	75	84	168		195	230	38	8

available only for GeS and GeSe up to now.(1,4). Using our reflectivity data and the literature 1 Raman data for GeS, we, have been able to correct Wiley's results. The values of splitting factors, Δ , are given in table 2 and the ratio of the intralayer and the interlayer force constants $(\frac{v_e}{\Delta})^2$ were calculated.

TABLE II

Splitting	v_e	v_i	v_o	Δ	$(v_e/\Delta)^2$
$\Gamma_{1u} - A_g$	315	269	292	118	6
$\Gamma_{1u} - A_g$	258	238	248	71	12
$\Gamma_{1u} - A_g$	118	111	115	28	16

Comparing the obtained data for this ratio which appears to be between 6 and 16 with Wiley's results (12-24) we conclude

that GeS is less layer-like than it was thought (1). In a similar way we have calculated that the ratio of the force constants for GeSe is between 17 and 175 which means that GeSe is much more anisotropic than GeS. It was very difficult to obtain any reliable Raman results for either SnS or SnSe so that we have not been able to compare them with Ge chalcogenides.

References

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