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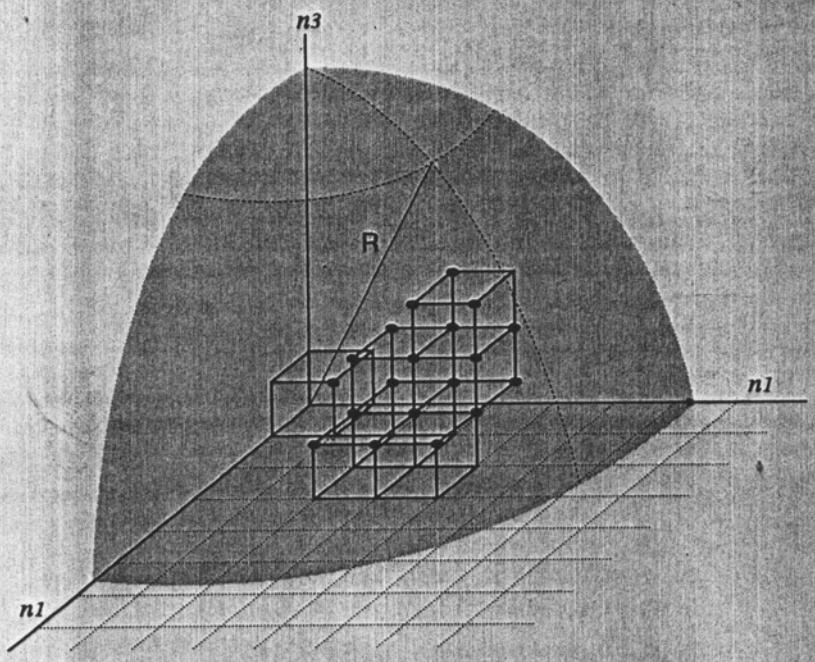

Dedicated to

Prof. Dr. N.A. Economou

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EXCITONIC AND OTHER INTERBAND TRANSITIONS IN $TlInS_2$ SINGLE CRYSTALS

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ABSTRACT

A study of the optical properties of the layered compound $TlInS_2$ is presented. Reflection spectra were measured at room temperature, in the energy region 1.5-6.2 eV. Transmission spectra were measured in the temperature range 10-290 K, in the energy region 1.5-3.5 eV. Two structures, at energy positions 2.57 and 2.87 eV (10 K), are attributed to transitions to the ground exciton state, from valence states split because of the spin-orbit interaction, at the point Γ of the Brillouin zone. Two other structures at higher energies are attributed to transitions at M_0 and M_3 critical points, respectively. Lorentzian line shapes are used to fit the structures of excitonic origin. The temperature dependence of the peaks and their broadening parameters are also presented.

I. INTRODUCTION

$TlInS_2$ belongs to the interesting group $A^{III}B^{II}C_2^{VI}$ chalcogenide semiconductors. It was first considered to have a tetragonal structure.[1] Later investigations classify the crystal to the monoclinic system.[2,3,4] Polytypical modifications with other crystal structures have also been reported.[5] This compound has attracted a widespread attention for its structural,[4] electrical,[6,7] photoconductive and holographic[8] properties. Optical spectra in the region of fundamental absorption,[9,10] Raman studies[3] and infrared reflection spectra[2] have also been published.

Inspite of the availability of the above results, the band structure of $TlInS_2$ has not been established, at least to the best knowledge of the present authors. In this work we present measurements of the optical transmission of $TlInS_2$ single crystals in the energy region 1.5-3.5 eV and in the temperature range 10-290 K. A reflection spectrum from 1.5 to 6.2 eV, obtained at room temperature, is also presented. The purpose of this work is to examine the structure of the spectra in the region of interband transitions, in order to obtain information about the nature of the critical points (CP's), their energy positions and the temperature dependence of their parameters. It is interesting, also, to further investigate the existence of excitonic effects, reported to occur in the vicinity of fundamental absorption.[10]

II. EXPERIMENTAL DETAILS

$TlInS_2$ single crystals were grown from their constituent elements Tl, In and S by chemical reaction in quartz ampoules and at a temperature of 800 °C. The resulting crystals have mirror-like surfaces and an average size of 5x3x0.5 mm^3. The structural characterization of the specimens used in our measurements was performed by means of transmission electron microscopy. Taking also into account structural investigations performed by other authors,[3,4] we interprete our TEM results as originating from the projection of a monoclinic cell with a=b=10.8 Å. The formation of twins in this compound has the result of practically doubling a c-axis length of about 15 Å.

Transmission and reflection experiments were performed using a double beam spectrophotometer with a prism-grating combination, that allows a resolution of 0.2 nm at 400nm. A liquid He cryogenic system, adapted to the spectrophotometer, enabled transmission measurements from 10K to 290K. The transmission was measured using a beam of unpolarized light incident normal to the crystal cleavage planes. The ordinary absorption coefficient was, thus, determined. The reflection was measured using a V-W optical configuration that enables the measurement of the absolute reflection of the specimens at near normal incidence.

The absorption coefficient was measured using very thin samples, prepared by repeated cleaving, using transparent adhesive tape. Very pronounced structures can be observed in transmission spectra, obtained with very thin samples (1-4 μm). Measurements of thicker samples (>10μm) result in smoothed peaks and eventually in a saturation of the absorption coefficient, in the energy region after 2.5 eV, following the fundamental absorption. Similar thickness dependent results were obtained in the region of interband transitions of GaSe.[11]

III. RESULTS

The reflection of $TlInS_2$ measured at room temperature, in the region 1.5-6.2 eV, is shown in Fig.1. A number of structures can be observed in this spectrum. Structure A, at lower energies, is obviously associated with transitions at the fundamental direct gap. The other structures, at higher energies, will be discussed later, taking into account the respective peaks of the absorption spectra.

Transmission measurements were used to determine the values of the absorption coefficient of the compound. Interference effects in the transparent region lead to the determination of the thickness of the sample. For this purpose, the long wavelength value of the refractive index, n=2.65 was used, obtained directly from reflection.

Fig. 2 shows the absorption coefficient α at temperatures 10 K and 290 K, in the photon energy region 1.5 to 3.5 eV. The values of the absorption coefficient, in the region of fundamental absorption, are considerably higher than values previously reported in the literature.[10] Two Lorentzian shaped peaks of strong absorption are shown to dominate in the low temperature spectrum. They are labeled A and B, in Fig.2. Their energy position is 2.58 and 2.87 eV, respectively. Structure A is attributed to direct optical transitions to the ground exciton state at the fundamental gap. Structure B is also considered to be of excitonic origin and as will be discussed later, can be associated with the spin-orbit splitting of the valence band at the center of the Brillouin zone. A third broad structure, labeled as structure C, is also evident in the absorption spectra. This peak, obviously is not related to exciton formation, since its intensity is not increased at lower temperatures. It will be attributed to transitions at an M_0 two dimensional (2D) critical point (see section IV b).

Peaks A, B and C have their corresponding structures in the reflection spectrum (Fig. 1). Structure D, in reflection, is not observed in absorption, since our transmission measurement is limited below 3.5 eV.

Technical reasons did not allow a direct measurement of the reflection at low temperatures. Therefore, we tried to determine the temperature variation of the refractive index measuring the shift of interference maxima and minima of transmission. It was found that the refractive index varies only very slowly with temperature. This dependence was roughly taken into account, where needed, in the analysis of the low temperature data.

IV. ANALYSIS AND INTERPRETATION OF THE OPTICAL SPECTRA.

a. Analysis of the second derivative spectra.

To obtain better information about the origin and the behavior of the observed peaks, an analysis of the optical spectra was performed, based on a fitting of the second derivatives of the dielectric function.

It is well known that singularities in the joint density of states at points of equal slopes of the valence and conduction bands, result in critical point absorption, giving rise to structures in the optical spectra. The complex dielectric function $\tilde{\varepsilon}(\omega)$ in the region of a critical point is given by the formula[12]

$$\tilde{\varepsilon}(\omega)= C-Ae^{i\Phi}(\omega-E+i\Gamma)^n \qquad (1)$$

where A, E, Γ are the strength of the transition, the critical energy and the broadening parameter, respectively. The exponent n and the phase φ determine the type and dimentionality of the critical point.

We can determine the critical point parameters by fitting the numerically obtained second derivatives of the experimental spectra, $d^2\varepsilon/d\omega^2$. The second derivatives were calculated using spline functions that smoothed without distording the lineshapes. The fitting was performed using a least square procedure.

In Fig. 3 the experimental second derivative of the imaginary dielectric function at T=70 K is shown with black dots. ε_2 is calculated through the equation

$$\varepsilon_2 = 2nk \qquad (2)$$

where n is the refractive index and k the extinction coefficient.

The fitting produced for structures A and B is satisfactory. A typical example for T=70 K is shown in Fig. 3 (solid line). The representation of the first structure with excitonic line shapes is good up to 200K. At higher temperatures an M_0 2D critical point line shape can better represent the experimental data. The second excitonic structure is well defined up to 150 K, while at higher temperatures is very poorly resolved.

Structure C in the second derivative of Fig. 3 is described as an M_0 two-dimensional critical point.

b. Temperature dependence of the critical energies and broadening parameters

Fitting the second derivative spectra at each temperature we deduce the critical point parameters A, E, Γ, φ. However, taking into account the uncertainty inherent in a multiparameter fitting of a second derivative spectrum and the nature of the performed measurements, we prefer to restrict ourselves in the presentation of the energy threshold E of the transitions and their broadening parameters Γ.

Fig.4 shows the temperature dependence of the critical energies E of the three peaks A, B and C found in the absorption spectra. The gaps depend linearly on temperature in most of the temperature range, while at low temperatures a quadratic dependence can be observed.

We attempt to describe the temperature dependence of the energy thresholds using Varshni's empirical law[13]:

$$E(T)=E(0)-\alpha T^2/(T+\beta) \qquad (3)$$

where α is the average temperature coefficient dE/dT and β has a value related to the Debye temperature of the material. The least square fitting of the experimental points using eq. (3), is shown in Fig.4 with solid lines. The temperature coefficient α is found equal to -5.4×10^{-4} eV/K

It is well known that the temperature variation of interband gaps can be attributed to the lattice dilatation, due to thermal expansion, and to electron-phonon interaction. A Bose-Einstein statistical factor for phonons with an average frequency Θ can , thus, be used to describe the observed variation of the energy threshold.[14] The fitting produced is in coincidence with the solid curve in Fig. 4, produced by the Varshni relation.

As shown in Fig.4 the values of the energy threshold of the second absorption peak, B, run almost parallel to those of the first peak. The second curve is displaced by a constant shift Δ of about 0.290 eV. The temperature coefficients of the two structures are found almost equal, within experimental deviations. These results, as well as the common excitonic origin of the two peaks, support our consideration that structure B is associated with transitions from a split off valence band at point Γ of the Brillouin zone.

The broadening parameters Γ of the two peaks A and B are shown in Fig. 5. As expected, broadening is increased with increasing temperature. To describe the dependence on temperature of the broadening parameters Γ of the two excitonic structures, again a Bose-Einstein statistical factor is employed:[14]

$$\Gamma(T)=\Gamma_0\left(1+\frac{2}{e^{\theta/T}-1}\right)+\Gamma_1 \qquad (4)$$

The best fit of experimental values is shown in Fig. 5 with solid lines.

V. CONCLUSIONS

The absorption coefficient at different temperatures for the layered compound $TlInS_2$ is presented in a region including transitions at the fundamental gap and other interband transitions up to 3.5 eV. At 10 K the fundamental gap is transformed into a fine exciton peak with Lorentzian line shape, appearing at 2.57 eV. Beside the ground state exciton transitions, the spin orbit splitting of the valence band at point Γ is resolved as a second exciton peak, found at 2.87 eV at 10 K . The valence band separation at the center of the Brillouin zone is Δ=0.290 eV. A third peak, appearing at 3.04 eV (10K) is attributed to transitions at an M_0 two dimensional critical point, on the basis of an analysis of the second derivative spectra with standard analytic line shapes.

Finally, a fourth structure at about 4.0 eV is resolved in the reflection spectrum and attributed to M_3 2D transitions.

Work on the intrinsic absorption spectrum of other similar chalcogenide compounds is under way. Similarities and differences between them will be discussed in a later publication.

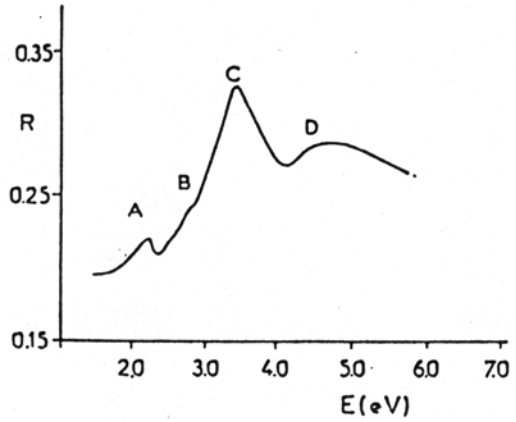

FIG. 1 : Reflection spectrum of $TlInS_2$ at room temperature.

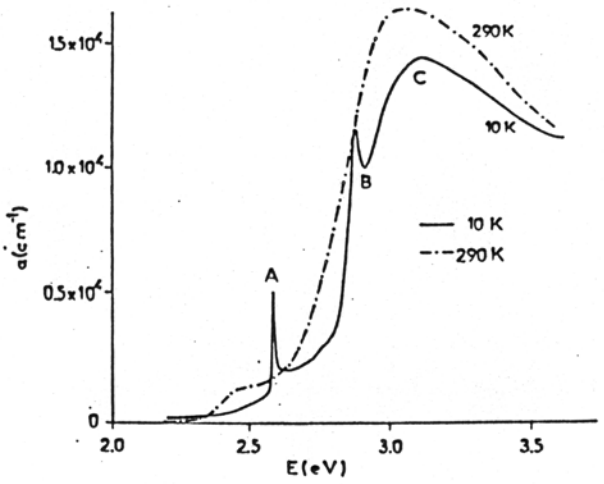

FIG. 2 : The values of the absorption coefficient versus photon energy at temperatures 10 K and 290 K.

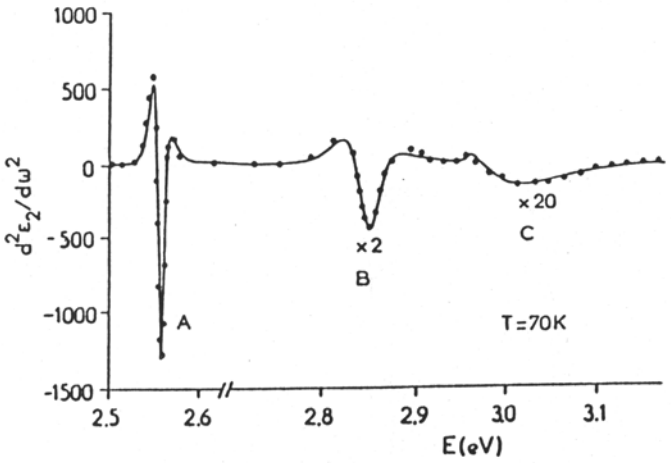

FIG. 3 : Second derivative of the imaginary part of the dielectric function (black dots), and the least square fitting (solid line), at T=70 K.

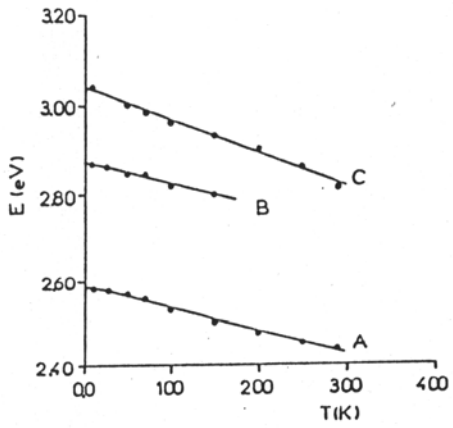

FIG. 4: Temperature variation of the critical energies of the three absorption peaks. Solid lines represent fittings produced with eq. (3).

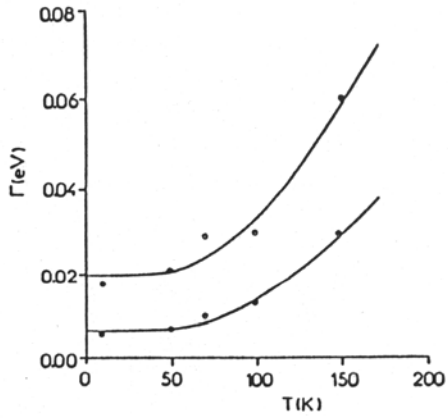

FIG. 5: Temperature variation of the broadening parameters Γ for the two excitonic peaks, A (lower curve) and B (upper curve). Solid lines represent fittings produced using eq. (4).

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