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Elliott's model and thermoreflectivity: Application to the layered structure $ZrSe_3$

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The Elliott model has found widespread use in the analysis of semiconductor absorption data. In this work, its application has been extended to reflectivity and, in particular, to thermoreflectivity data. The layered semiconducting compound $ZrSe_3$ is a suitable material for such a study, since its structure produces a negligible surface effect, thus facilitating the analysis. Good-quality single crystals were grown and the thermoreflectivity was measured between 40 K and room temperature. Taking into account both the band and exciton contributions, an excellent fit was obtained allowing a characterization of the excitons in $ZrSe_3$. A large exciton binding energy was found (49 meV) along with a large value of the coupling constant, illustrating the importance of the electron-phonon interaction in this material.

INTRODUCTION

It has been established for several years that the Elliott model,[1] adapted for direct applications,[2-4] gives an excellent description of an M_0 critical point in the presence of electron-hole interactions in the case of parabolic bands. These interactions, as in the hydrogen atom, lead to the appearance of discrete levels (i.e., bound states) in the gap near the conduction-band minimum, and to an increase in the absorption due to nonbound states in the continuum region. However the agreement with experiment has not always been easy. The observed behavior often differs significantly from what one would expect. Attempts to explain these deviations have shown the importance of surface effects.[5-8]

When the transition presents an excitonic character as dealt with in the Elliott model, the most dramatic surface effect is the formation of a so-called "dead layer." The high sensitivity of reflectivity spectra to an applied electric field in the case of GaAs (Ref. 6) and InP (Ref. 7), for example, helped in understanding the origin of this effect. Although it has been expressed differently in the past, we believe that the dead layer is related to a surface reconstruction resulting from incomplete bonds and leading to the appearance of a surface potential whose value depends on the Fermi energy which in turn is determined by the density of deep traps and their activation energy. This surface potential repels or dissociates the exciton up to a certain distance. An interference phenomenon is thus produced in the reflectivity spectrum near the transition energy due to the difference in the indices of refraction of the dead layer and the bulk. The application of an electric field acts directly on the potential and therefore on the thickness of the dead layer. As one moves away from the transition energy, the indices of refraction become identical and the interference disappears.

In the case of layered compounds, one expects surface effects to be relatively weak for two main reasons. First, it is easy to cleave these materials parallel to the layers and to work with surfaces free of contamination from the environment. More importantly, however, the covalent bonds act within each layer, the cohesion of the layers depending only on van der Waals forces. Therefore any surface potential will be weak or nonexistent. Obviously the samples must be of excellent quality to avoid other types of perturbation.

The only layered compounds that have been subjected to the Elliott model are GaSe (Ref. 9) and InSe (Ref. 10). Absorption measurements were involved and a quantitative fit was obtained for both the discrete and continuum regions of the spectrum. This is an interesting result in that not only the exciton binding energy and other parameters were determined, but the matter of the dimensionality of the exciton was cleared up. It is now established that the exciton is three dimensional in these two compounds.

$ZrSe_3$-type compounds are semiconductors and belong to the family of layered materials. Their anisotropy, however, is larger than that of GaSe and InSe. They have been the subject of several publications describing results of Raman and infrared spectroscopy[11-15] on one hand, and visible spectroscopy[16-20] on the other. In the former, different models for the representation of interatomic forces have been proposed to account for the experimental data and to estimate the degree of interchain coupling. In the latter, a characterization of different electronic transitions has been made. It is now known that the fundamental gap is indirect and that the direct gap presents strong excitonic effects. The characteristics of the exciton, however, are unknown.

Contributing to knowledge in this field is interesting since a certain analogy exists between these compounds and similar artificial structures such as superlattices.

Thermoreflectance (TR) is one of the modulation techniques and is known as a powerful tool to localize and identify critical points in the Brillouin zone.[21] Except for wavelength modulation, it is the only one which is scalar in nature. It is easy to use but the interpretations have not always been sufficiently rigorous due in part to the approaches used and to the technique inself. The object of this paper is to determine to what degree one can characterize the exciton by this technique, going beyond what has been done in the past. Although the application will be made to $ZrSe_3$, a broader scope is envisioned. We therefore wish to find exactly what the Elliott model predicts for the TR and to confront it with experimental results. We will begin by describing the approach used and illustrate the different contributions. Then the experimental results will be presented and discussed. Finally, an interpretation of the results obtained as a function of temperature as required by the analysis will be presented.

ELLIOTT'S MODEL AND THERMOREFLECTIVITY

Preliminary considerations (Lorentz model)

An alternative to the Elliott model which in certain cases may constitute a good approximation is the Lorentz model. The latter implies a simple transition centered at an energy E_0 with a broadening parameter Γ, and gives a dielectric constant

$$\epsilon(E)=\epsilon_b+\frac{4\pi\alpha E_0^2}{E_0^2-E^2-ie\Gamma} ,$$

where α is the polarizability of the exciton and ϵ_b the background dielectric constant. This approach found widespread use in the literature following Batz[22] who first applied it in a thorough analysis of TR results. By taking into account the effects of the dead layer, the reflectivity data of GaAs (Refs. 5 and 6) and InP (Ref. 7) were also successfully fitted in light of this model. Later the same procedure was applied to the TR data of ZrS_3 and $ZrSe_3$ (Ref. 23) but for reasons mentioned above, we believe that this procedure is not quite justified. In contrast, for GaAs and InP, the interference due to the dead layer completely dominates the spectrum and use of the Elliott model would have had a minor but probably beneficial effect, since the author mentioned that slight differences still existed between theory and the fitted spectrum.

Nevertheless, this model is an approximation. It neglects the excitonic levels beyond $n=1$ as well as the absorption due to the band and to nonbound exciton states. Therefore it can in no way characterize the exciton. To obtain the binding energy, etc., one must resort to a more sophisticated model.

Thermoreflectivity (Elliott's model)

As a starting point, let us choose the most practical version of the model as formulated by various authors.[4,9,10] This version is directly applicable to absorption measurements with the absorption coefficient given by

$$\alpha(E)=\frac{2A_mR_e^{1/2}}{nE}\left[\sum_l -\frac{R_e}{l^3}\frac{\Gamma_l/2+b(E-E_l)}{(E-E_l)^2+(\Gamma_l/2)^2}+\int_{E_g}^{\infty}\frac{\Gamma_c/2}{(E'-E)^2+(\Gamma_c/2)^2}\,\frac{1}{1-\exp[-2\pi R_e^{1/2}(E'-E_g)^{-1/2}]}dE'\right] , \tag{1}$$

where the lth excitonic level has an energy $E_l=E_g-R_e/l^2$, R_e represents the exciton binding energy, n the index of refraction, Γ the broadening parameter, and E_g, the energy gap. A_m is a constant related to the reduced effective mass (μ) and to the matrix element $|M|$ of the transition,

$$A_m=\frac{2\pi(2\mu)^{3/2}e^2|M|^2}{c\hbar^2m_0^2} .$$

This formulation implies a matrix element independent of energy, an arbitrary choice, which however avoids further complications. An alternative would be to assume a constant oscillator strength $f_{cv}=2|M|^2/m_0E$, which it turns out, leads to an inferior fit with experiment. The parameter b appears in the literature to account for small assymetries observed experimentally and takes on very small values.[9,10] In our case it was taken equal to zero since no effect was detected for such values.

It should also be pointed out that our attempts to measure directly the absorption of 1-μm-thick samples were unsuccessful. Although some chalcogenides can be cleaved to still smaller thicknesses, in this case, it was not possible while maintaining good crystal quality. The transmitted signal approached the noise level for α values estimated at 30 000 cm^{-1} before reaching the energy of the structures observed in TR. In fact, as will be shown below, the absorption coefficient reaches values of $\approx 10^6$ cm^{-1} near the transition energy and would have required thicknesses of a few hundred angstroms. Since such thicknesses are unattainable, our approach is justified.

Equation (1) may be rewritten in the form

$$\alpha(E)=\frac{1}{n}f(E;A_m,R_e,\Gamma,E_g) . \tag{2}$$

In fitting the spectra, E_g must account for the energy of a transition and Γ for its broadening. Thus A_m and R_e are in effect the only adjustable parameters. If α did not vary appreciably, n could have been assumed constant and included in A_m. Since this is not the case, we shall write an analogous equation for the imaginary part of the dielectric constant

$$\epsilon_2(E)=\frac{\hbar c}{E}f(E;A_m,R_e,\Gamma,E_g) \tag{3}$$

since $\epsilon_2(E)$ is given by $(\hbar c/E)n\alpha$.

Then ϵ_1 can be obtained through the Kramers-Kronig relation

$$\epsilon_1(E)=\epsilon_R+\frac{2}{\pi}\int_0^\infty \frac{E'\epsilon_2(E')}{E'^2-E^2}dE' \ .$$

In the literature, one finds 1 or $\epsilon(\infty)$ instead of ϵ_R. The value 1 is used whenever ϵ_2 is known for all frequencies. ϵ_1 is then also determined for all frequencies. If the study only involves the far infrared, one must use $\epsilon(\infty)$ to take into account all electronic transitions. Our case is an intermediate one since only part of the electronic transitions are considered. ϵ_R is chosen such that the calculated value of n in the region of transparency corresponds to the measured one in that region. There is, however, no physical significance for the ϵ_R so obtained since it depends on the interval of integration and on the strength of the considered transition with respect to the others. ϵ_1 and ϵ_2 being determined, one can calculate R which can also be expressed in terms of n and k:

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}=R(E;A_m,R_e,\Gamma,E_g) \ .$$

In TR measurements, all parameters which depend on temperature are modulated. Most authors assume that R_e is temperature independent.[10,24,25] Since A_m is also constant, only E_g and Γ are modulated, so that the variation in reflectivity is

$$\begin{aligned}\Delta R&=\frac{\partial R}{\partial E_g}\Delta E_g+\frac{\partial R}{\partial \Gamma}\Delta\Gamma\\&=\frac{\partial R}{\partial E_g}\frac{dE_g}{dT}\Delta T+\frac{\partial R}{\partial \Gamma}\frac{d\Gamma}{dT}\Delta T\end{aligned}$$

for small ΔT. The measured quantity is actually $\Delta R/R$ and since dE_g/dT is negative and $d\Gamma/dT$ positive, this may be expressed in the following form, the relevance of which will become apparent in what follows:

$$\frac{\Delta R}{R}=\left[-\frac{1}{R}\frac{\partial R}{\partial E_g}+\frac{1}{R}\frac{\partial R}{\partial \Gamma}\frac{d\Gamma/dT}{|dE_g/dT|}\right]\left|\frac{dE_g}{dT}\right|\Delta T \ . \tag{4}$$

Analysis

The objective is to use the Elliott model to predict an optical spectrum and compare it with experimental results. In doing so, one encounters several problems which are described by the following remarks.

(1) The model itself does not predict the behavior of all the factors in Eq. (4) (e.g., $d\Gamma/dT$ and dE_g/dT must be determined experimentally).

(2) The data must be obtained as a function of temperature and the fitting procedure must be done in a self-consistent manner. Even a fit at a given temperature requires $d\Gamma/dT$ and thus fits at neighboring temperatures.

(3) The amplitude of $\Delta R/R$ is not known, since ΔT is not. Furthermore ΔT varies with temperature.

(4) One must be cautious in using tables describing the behavior of optical parameters near critical points. For example, the transition may or may not have an excitonic character. Moreover a large value of R_e/Γ leads to a more complex structure. Other factors may come into play, depending on the crystal and its quality.

In light of the above remarks, the following procedure was adopted. TR spectra were obtained at various temperatures between 30 and 300 K. An initial fit for different values of the ratio $(d\Gamma/dT)(dE_g/dT)$ was performed at each temperature to evaluate the range of variations of Γ and E_g. This step was repeated to further define these variations before proceeding with the final step. The uncertainty in the amplitude of the signal due to that in ΔT is problematic since replacing R by aR^b in Eq. (4) will only bring about changes in the amplitude. It can be shown that this problem can be resolved if one has a value of the reflectivity or absorption near the transition at a single temperature and wavelength so that the fit will reproduce it. For a clearer demonstration, we have performed a fit of the reflectivity at low temperatures (30 K) where the spectrum presents a more detailed structure.

Once the amplitude has been accounted for, the relevant quantity is the one in large parentheses in Eq. (4). To illustrate the behavior, we chose parameter values of the same order of magnitude as those eventually found for ZrSe$_3$: $\Gamma=0.025$ eV, $E_g=2.0$ eV, $R_e=0.060$ eV, $\epsilon_r=9$. The length of the calculations did not allow a systematic study of the effect of varying these parameter values.

The calculated absorption coefficient (Fig. 1) is typical of the measured coefficients for different types of compounds.[4,9,10] This is not the case for the reflectivity (Fig. 2) for which a comparison is more difficult. The most studied compounds (III-V and II-VI semiconductors) as mentioned above are sensitive to surface effects. For this reason, the Elliott model has generally been restricted to the analysis of absorption measurements. On the other hand, no thorough study has been undertaken for layered compounds.

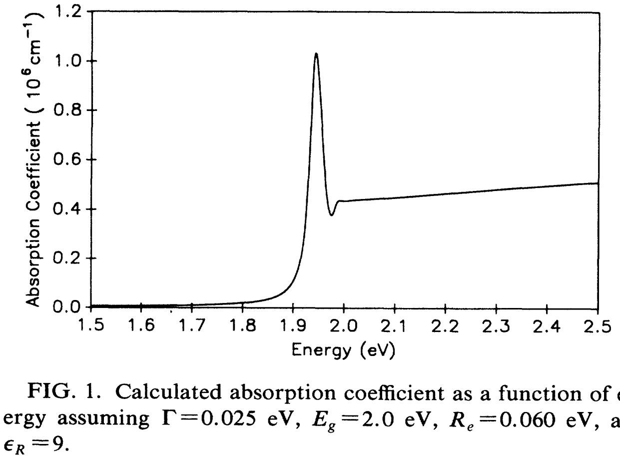

FIG. 1. Calculated absorption coefficient as a function of energy assuming $\Gamma=0.025$ eV, $E_g=2.0$ eV, $R_e=0.060$ eV, and $\epsilon_R=9$.

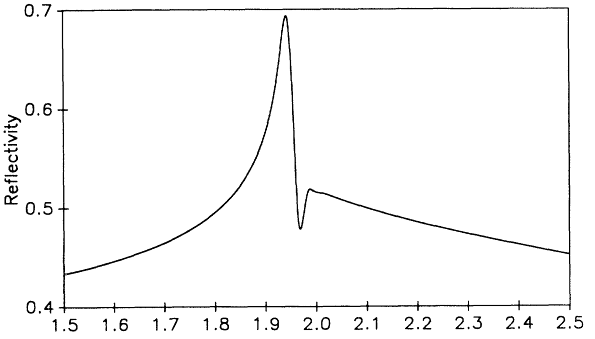

FIG. 2. Calculated reflectivity as a function of energy assuming the parameters of Fig. 1.

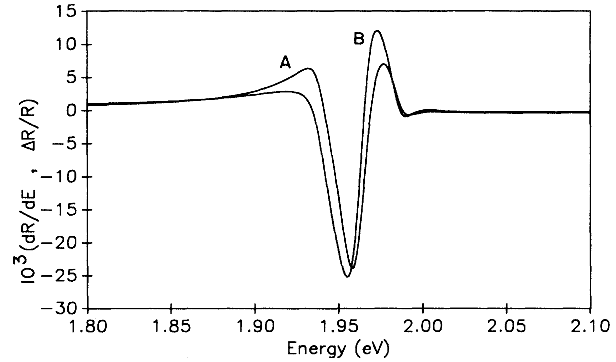

FIG. 4. The wavelength modulation (A) and thermoreflectivity (B) as a function of energy assuming the parameters of Fig. 1.

Figure 3 shows the three main contributions to the TR:

$$-\frac{1}{R}\frac{\partial R}{\partial E_g},\ \left[\frac{1}{R}\frac{\partial R}{\partial \Gamma}\right]_{\text{exciton}},\ \left[\frac{1}{R}\frac{\partial R}{\partial \Gamma}\right]_{\text{band}}.$$

For clarity, the exciton and band contributions are shown separately even though identical values were chosen for the two broadening parameters. It is worth noting that the contributions involving Γ are not at all negligible as suggested by a number of publications. In addition, they are multiplied by the ratio $(d\Gamma/dT)/(dE_g/dT)$ which may be larger than unity. (In $ZrSe_3$ it is ≈ 1.3.)

Finally, the TR is illustrated in Fig. 4 and compared to wavelength modulation. Significant differences in shape are observed along with a small shift of the minimum of the structure. These differences are all due to the Γ contributions. In fact, calculations lead to practically identical results for $\partial R/\partial E$ and $-\partial R/\partial E_g$. This is not obvious from Eq. (1) as it is from the original formulation of the Elliott model.

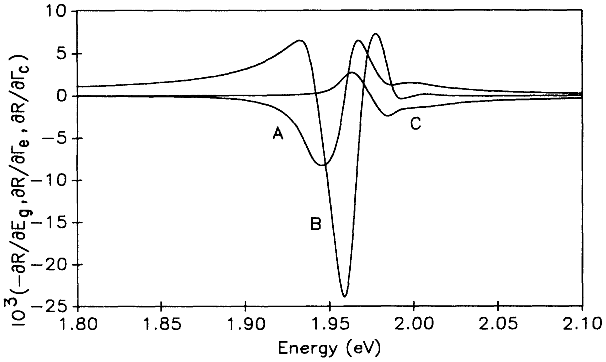

FIG. 3. The three main contributions to the thermoreflectivity as a function of energy assuming the parameters of Fig. 1. A, $-\partial R/\partial E_g$; B, $\partial R/\partial \Gamma_e$; C, $\partial R/\partial \Gamma_c$.

APPLICATION TO $ZrSe_3$

Experimental techniques

The single crystals were obtained by the well-known vapor-transport technique. The case of $ZrSe_3$ reported here is part of a more general project involving $HfSe_3$ and $Hf_xZr_{1-x}Se_3$ alloys. Adding a small amount of water to the iodine-transport agent led to an improvement in the size and quality of the crystals. Such a procedure has never been reported in the literature. It appears that water acts directly on the kinetics of the crystal growth slowing down significantly the reaction process with subsequent improvements.

The best crystals were selected and only those with excellent freshly cleaved surfaces were studied. Their thickness was typically 10–20 μm. The TR measurements were performed on a standard setup similar to the one mentioned in Refs. 23 and 26. The same setup was used for the reflectivity measurements. The latter are more demanding and required among other things improvements in the pumping system since residual gases can condense on the sample thereby modifying the reflectivity. In the case of TR measurements, the ratio $\Delta R/R$ is much less sensitive to this phenomenon.

Results

The TR spectrum of $ZrSe_3$ between 1.4 and 3.6 eV contains four well-defined structures for $\mathbf{E}\|\mathbf{b}$ axis (Fig. 5). Apart from the increased broadening at higher energies, they are quite similar, and considering their intensities are all probably due to direct transitions. None of these structures are observed with $\mathbf{E}\perp\mathbf{b}$ axis as shown by the lower curve which has already been published.[23] Instead, a few diffuse meaningless structures appear due to the inferior quality of the samples and experimental setup available at that time. Thus only spectra corresponding to $\mathbf{E}\|\mathbf{b}$ will be presented below. All our attempts to detect an indirect gap failed although such a transition is easily observable in ZrS_3, for example. This does not exclude the possible existence of such a gap in $ZrSe_3$. Reflectivity and even modulated reflectivity measure-

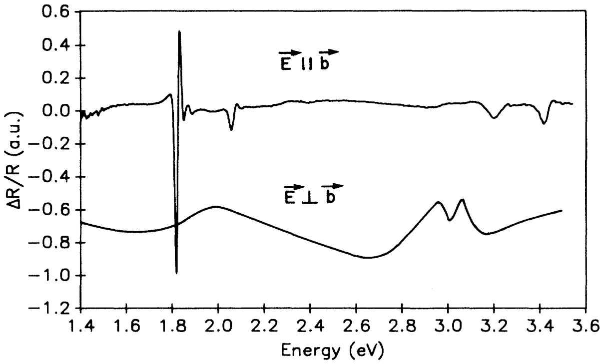

FIG. 5. The thermoreflectivity of $ZrSe_3$ as a function of energy at 30 K for two polarizations. The lower curve was centered about zero before being translated vertically for clarity.

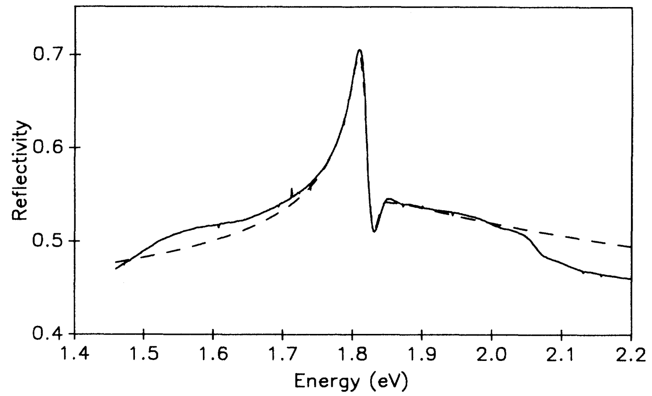

FIG. 7. The measured and calculated reflectivity of $ZrSe_3$ assuming the parameters obtained in Fig. 6.

ments may be completely insensitive to relatively small variations in absorption.

Apart from the indirect gap, the behavior observed in Fig. 5 is typical of all available TR spectra of transition-metal trichalcogenides. The relative and absolute positions of the transitions may of course differ. In what follows we will focus our attention on the main transition which may be seen more closely in Fig. 6. This transition has been associated with the lowest direct gap of $ZrSe_3$ (Refs. 16 and 27) and its pronounced excitonic character makes it appropriate for a confrontation with the Elliott model. Its general shape is the same as that reported by other authors for this[23] and similar compounds.[23,24] In fact, one may even generalize this result for all semiconducting compounds of the transition-metal trichalcogenides family. A closer look at the structure for different samples, however, indicates differences in the amplitude ratio of the positive and negative peaks. These differences are related to the crystal quality. The structure of Fig. 6 corresponds to our best crystal and has the highest ratio ever reported.

The observed spectrum behaves exactly as that predicted by the model (Fig. 4). For that matter, Fig. 6 shows a fit along with the corresponding parameter values. The quality of the fit is quite good despite the rigidity of the model. In cases where a dead layer is considered, the thickness allows a significant variation of behavior while the other parameters remain constant. Here only the ratio R_e/Γ can directly affect the shape of the structure.

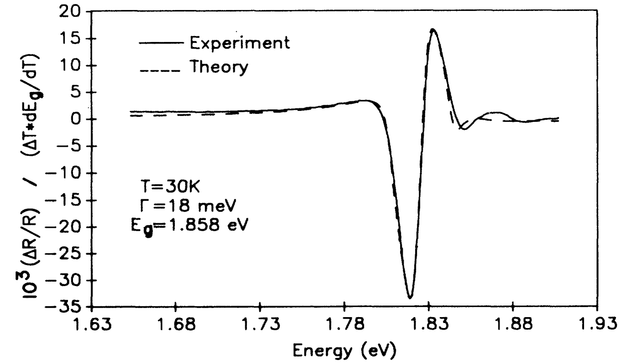

FIG. 6. The measured and calculated thermoreflectivity of $ZrSe_3$ as a function of energy near the fundamental gap at 30 K with **E**∥**b**.

According to Eq. (4), the value chosen for $(d\Gamma/dT)/(dE_g/dT)$ allows one to adjust the amplitude ratio of the positive and negative peaks but this value must be consistent with the fits done at different temperatures as shown in Fig. 8. Here also, the experimental results follow closely the model whereas only Γ and E_g have been readjusted. One can also see how the shape is affected as R_e/Γ decreases. Finally, to verify the validity of the parameter values following the amplitude problem in the TR, Fig. 7 shows the measured reflectivity and the one calculated with the parameters obtained from the TR fit of Fig. 6. The experimental spectrum was normalized using the measured index of refraction in the transparency region. The theoretical spectrum was adjusted through ϵ_R which allows one to raise or lower the curve so that it coincides with the experimental one. The excellent agreement shows the coherence of the treatment. As noted above, it is only necessary to reproduce the value of the absorption or reflectivity at one point in the immediate vicinity of the transition.

DISCUSSION

TR spectra

The values obtained for the parameters differ appreciably from the ones usually encountered.[4,5,7,9,10] The large anisotropy in $ZrSe_3$ is undoubtedly responsible for the differences. The tendency towards larger values of R_e and Γ has already been pointed out for the less anisotropic materials of GaSe (Ref. 9) and InSe.[10] The exact role of this anisotropy in the increase of R_e is still obscure. Regarding Γ, it is known that the nature of the material favors a large electron-phonon interaction. It will be shown that a model based only on this type of interaction leads to the observed values and their variation with temperature.

The role of Γ in the fitting procedure is clear since it determines the width of the structure but that of R_e is less obvious. Nevertheless in our attempts to fit the data we found that the value of R_e is directly related to the energy difference between the maximum and minimum of the observed structure both in reflectivity and in TR. With the quality of the fit obtained, this yields an uncertainty of approximately 1 meV. The simultaneous fit of the reflectivity and the TR ensures the validity of A_m.

The model is three dimensional and implies the following relations:

$$E_l = E_g - \frac{R_e}{l^2}, \quad R_e = \frac{\mu}{m_0}\frac{R_H}{\epsilon^2}, \quad a_0^* = \frac{\epsilon m_0 a_0}{\mu},$$

where m_0 is the electron mass, a_0 the Bohr radius, R_H the Rydberg constant, a_0^* the exciton Bohr radius, μ its reduced mass, and ϵ the dielectric constant.

Using our result for R_e along with the last two relations

$$a_0^* = \frac{283 a_0}{\epsilon}.$$

The problem now is to choose a value for ϵ. If a_0^* is relatively large and includes several unit cells as is generally the case, ϵ will be the static dielectric constant. If instead one uses the $\epsilon(\infty)$ value obtained with the index refraction in the transparency region, namely $\epsilon(\infty)=28$, one obtains $a_0^* = 10a_0$. The static dielectric constant is neces-

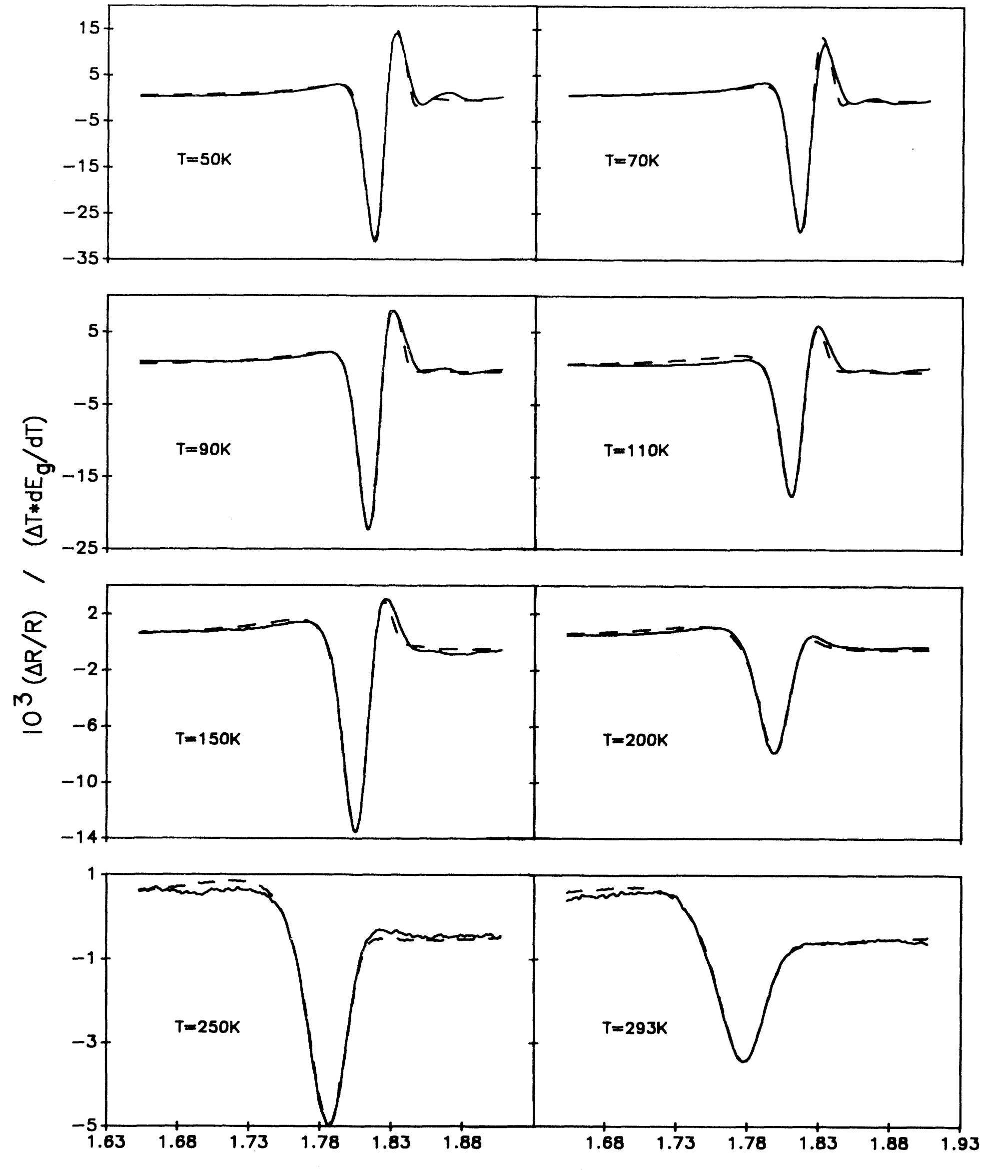

FIG. 8. Thermoreflectivity of $ZrSe_3$ as a function of energy for various temperatures.

sarily larger and may not be used since it leads to an a_0^* value that is even smaller. $\epsilon(\infty)$ probably constitutes a good compromise giving an exciton Bohr radius of the same order of magnitude as the unit cell. (The crystal is monoclinic with $a = 3.4109$ Å, $b = 3.7489$ Å, $c = 9.444$ Å, $\beta = 97.48°$, and there are eight atoms in the unit cell.)

It is clear that we are close to the limit of conditions describing a Wannier exciton which raises the question of the validity of our approach. Indeed, the formalism describing the Wannier exciton is based upon the effective-mass approximation and assumes parabolic conduction and valence bands. This is certainly not true over the whole Brillouin zone. If the exciton has a large radius, the uncertainty principle implies that only a small region of **k** space is sufficient to construct the wave functions. The approximation is therefore justified. On the other hand, if the radius is small, as in our case, one would expect that terms of order greater than two become significant in the development of energy versus k. However, the excellent agreement between theory and experiment tends to show that the model is still valid at least up to this limit. The reason may be the following: With the chosen value of the dielectric constant, one obtains a reduced effective mass of the order of $2.8m_0$, corresponding to extremely flat bands. These bands may then be considered parabolic over a larger fraction of the Brillouin zone.

Another aspect concerns the dimensionality. The model is three dimensional whereas the material is strongly anisotropic and quasi-two-dimensional. In fact, the anisotropy did have some effect, giving a large binding energy, a large reduced effective mass, and a small lifetime. Just how this compensates to maintain the three-dimensional nature requires further study. Nevertheless, with such physical properties, the excitons in $ZrSe_3$ are not suitable for the exploration of the dimensionality of the crystal. A two-dimensional model implies different positions and relative intensities of the exciton excited states and leads to an inferior fit with experiment. A characterization of the effective masses parallel and perpendicular to the c axis would also help clarify the situation.

Electron-photon interaction

The study of the TR as a function of temperature, as required by the analysis, allowed us to determine the corresponding variations of E_g and Γ. These are shown in Fig. 8. Let us recall that these constitute the only adjustable parameters as expected since A_m and R_e are constants characteristic of the material.

Several mechanisms are generally involved in the energy-gap variation with temperature.[28] In GaSe and InSe it is well established that the electron-phonon interaction dominates.[10,29,30] This is not surprising since this interaction is favored in layered structures. The effect should be even more pronounced in $ZrSe_3$ which has a lower crystal symmetry and a larger anisotropy.

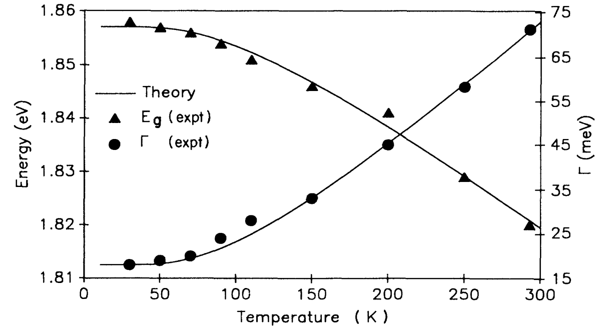

FIG. 9. The measured and calculated values of E_g and Γ as a function of temperature.

In the case of a short-range three-dimensional interaction involving an optical phonon, the contribution to the self-energy is[31]

$$\Delta E = -B(\hbar\Omega)^{1/2}N$$

with

$$B = \frac{8g\ln 2}{\pi}\sqrt{\hbar^2 Q^2/2m^*}\ ,$$

where $\hbar\Omega$ is the phonon energy, g a dimensionless electron-phonon coupling constant, m^* the effective mass of the carriers, Q an effective Brillouin zone radius, and N the phonon occupation number. The phonon-emission and -absorption processes are given by

$$\tau_e^{-1} = (2/\hbar)g^2(N+1)\sqrt{\hbar Q(\varepsilon - \hbar\Omega)}\ ,$$

$$\tau_a^{-1} = (2/\hbar)g^2 N\sqrt{\hbar\Omega(\varepsilon + \hbar\Omega)}\ ,$$

where ε is the kinetic energy associated with the k extension of excitonic wave functions. The curves of Fig. 9 describe the simultaneous fits obtained for E_g and Γ with the following values: $\hbar\Omega = 24.9$ meV, $g = 1.4$, $\varepsilon = 28.4$ meV, $B = 12.2$ $\text{meV}^{1/2}$. Again the excellent agreement between theory and experiment confirms the dominance of the electron-phonon interaction. This is also illustrated by the high value of the coupling constant g in comparison with that for InSe and GaSe ($g = 0.5$).

CONCLUSION

In the past, the Elliott model has essentially been confronted with absorption data. However such measurements are not always possible. We have extended its application to reflectivity and TR. In the latter case, a detailed analysis of the different contributions and the problems of interpretation were presented. In the general case, one must take into account surface effects. However, for layered compounds, the surface potential is weak and these effects are negligible. The excellent agreement obtained for $ZrSe_3$ confirms as expected the direct link between the surface potential and the dead layer both absent in $ZrSe_3$.

We have thus determined the characteristics of the main exciton in $ZrSe_3$ and cleared the way for the study of similar compounds. The analysis raised important questions regarding the dimensionality and the limits of validity of the model. It appears to remain applicable even when the exciton Bohr radius is of the same order of magnitude as the unit-cell dimensions, at least in this type of compound. We point out that localization effects may arise due to the dimensionality. The nature of the material which favors a strong electron-phonon interaction and the smallness of the exciton Bohr radius may also induce self-trapping effects. Finally, such large exciton binding energies are of interest in heterostructures because of the obvious devices possibilities.

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