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Influence of temperature and pressure on the electronic transitions in SnS and SnSe semiconductors

Martin Parenteau and Cosmo Carlone
Département de Physique and Centre de Recherche en Physique du Solide,
Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

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Optical-absorption measurements in the near infrared have enabled us to determine the direct and indirect band gaps of SnS and SnSe layered compounds, in the **a** and **b** polarizations, at temperatures ranging from 7 to 295 K (at $P=0$ kbar) and pressures up to 40 kbar (at $T=295$ K). At $T=295$ K and $P=0$ kbar, we obtain, for SnS, $E_{\mathrm{ind}\,\mathbf{a}}=1.076$ eV, $E_{\mathrm{ind}\,\mathbf{b}}=1.049$ eV, and $E_{\mathrm{dir}\,\mathbf{b}}=1.296$ eV; and for SnSe, $E_{\mathrm{ind}\,\mathbf{a}}=0.898$ eV, $E_{\mathrm{ind}\,\mathbf{b}}=0.903$ eV, $E_{\mathrm{dir}\,\mathbf{a}}=1.238$ eV, and $E_{\mathrm{dir}\,\mathbf{b}}=1.047$ eV. For both crystals, an additional structure, associated with an impurity level, is observed in the **a** polarization. Its shape reveals the three-dimensional nature of the electronic properties in these compounds. The measured pressure coefficients for the transitions $E_{\mathrm{ind}\,\mathbf{a}}$, $E_{\mathrm{ind}\,\mathbf{b}}$, $E_{\mathrm{dir}\,\mathbf{a}}$, and $E_{\mathrm{dir}\,\mathbf{b}}$ are, for SnS, -5.6, -6.0, -8.3, and -7.3 meV/kbar, respectively; and for SnSe, -5.2, -8.9, -3.6, and -11.2 meV/kbar, respectively. The corresponding temperature coefficients are, for SnS, -0.24, -0.36, . . . (undetermined), and -0.563 meV/K; and for SnSe, -0.32, -0.29, -0.43, and -0.43 meV/K. The behavior of the transition energies with temperature is explained by a self-energy correction attributed to the interaction between electrons and nonpolar phonons. Concerning this temperature dependence, we find that the effect of volume dilatation is opposite in sign to that of the electron-phonon interactions. The latter effect dominates.

I. INTRODUCTION

Recently, attention has been focused on the optical properties of layered semiconductors SnS and SnSe, notably because of their use in holographic-recording systems.[1] These IV-VI compounds crystallize in an orthorhombic structure[2] belonging to the space-group symmetry D_{2h}^{16} (*Pnma*). Their unit cell spans two layers, which stack along the **c** axis of the crystal.[3] Their first optical transitions for the **a** and **b** polarizations take place in the near infrared. The direct band gaps have been studied by means of electroreflectance and thermoreflectance measurements[4,5] as well as by absorption measurements.[6,7] The latter technique has also been used to observe indirect transitions.[6,8–12] However, considerable scatter is found among the proposed values for the electronic transition thresholds, and an absorption structure, observed in the **a** polarization,[7] has yet to be explained. Moreover, the behavior of the transition energies of these compounds as a function of pressure is not known and no study of the electron-phonon interaction has been carried out to date. A simultaneous study with temperature and pressure allows the separation of the effects of change of volume (implicit contribution) from those of electron-phonon interaction at a fixed volume (explicit contribution), both involved in the temperature dependence of transition energies.

These considerations induced us to undertake a systematic study of the behavior of electronic transitions in SnS and SnSe with pressure and temperature. In this paper, we present the results of measurements of the optical-absorption coefficient in the range of the first interband transitions. Firstly, the transition thresholds are measured and then, their pressure and temperature dependence is analyzed.

II. EXPERIMENT

SnS and SnSe compounds have been studied on the one hand by transmission, as a function of temperature (from 7 to 300 K at $P=0$ kbar) and pressure (up to 40 kbar at $T=295$ K), and on the other hand by reflectivity, as a function of temperature. The thickness of the samples obtained by cleavage along the **c** axis ranged from 2 to 100 μm for transmission measurements, and was greater than 500 μm for reflectivity measurements. A tungsten lamp, a Jarrell-Ash MonoSpec50 spectrometer and a detection system (a PbS crystal connected to a lock-in amplifier) permitted the measurement of the spectra. For all these measurements, the incident light was polarized parallel to the **a** or **b** axis of the crystals in the plane of the layers. The orientation of the samples was obtained by optical transmission, with the help of the well-known dichroism of these compounds.[6,8–12] For the measurements with the Bassett-type high-pressure cell,[13] paraffin oil was used as the hydrostatic pressure medium.[14]

III. ABSORPTION COEFFICIENT ANALYSIS

A. Theory

The model proposed by Dumke, Lorenz, and Pettit[15] for the absorption coefficient $\alpha(\hbar\omega)$ (as a function of photon energy $\hbar\omega$) allows one to determine both direct and indirect gaps simultaneously. Since it accounts for all of the absorption curve contained between these transition thresholds, it does not rely as much on the identification of every indirect transition process as do the usual methods.[6,11,16] This was a major asset for the analysis of our spectra, which did not show the expected breaks in the slope of the functions $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^{1/3}$, necessary for the usual analysis.

We consider the absorption due to indirect transitions assisted by the absorption or emission of phonons from the branch ℓ of constant energy $\hbar\Omega_\ell$ and population n_ℓ in a crystal with direct and indirect gaps being $E_{\rm dir}$ and $E_{\rm ind}$, respectively. The absorption coefficient is obtained from the formula (5) in Ref. 15 (C_i is a constant):

$$\alpha_{\text{absorption}\,\ell}(\hbar\omega)=\begin{cases}0 \quad \text{for } (\hbar\omega+\hbar\Omega_\ell)<E_{\rm ind}\\ \dfrac{C_i n_\ell(\hbar\omega+\hbar\Omega_\ell-E_{\rm ind})^2}{\hbar\omega(\hbar\omega-E_{\rm dir})g_-(g_-+1)^2} \quad \text{for } (\hbar\omega+\hbar\Omega_\ell)>E_{\rm ind}\,,\end{cases}$$

$$\alpha_{\text{emission}\,\ell}(\hbar\omega)=\begin{cases}0 \quad \text{for } (\hbar\omega-\hbar\Omega_\ell)<E_{\rm ind}\\ \dfrac{C_i(n_\ell+1)(\hbar\omega-\hbar\Omega_\ell-E_{\rm ind})^2}{\hbar\omega(\hbar\omega-E_{\rm dir})g_+(g_++1)^2} \quad \text{for } (\hbar\omega-\hbar\Omega_\ell)>E_{\rm ind}\,,\end{cases} \tag{1}$$

$$\text{where} \quad g_\pm^2=1+\frac{\left[1+\dfrac{m_v^*}{m_{c'}^*}\right][\hbar\omega-(E_{\rm ind}\pm\hbar\Omega_\ell)]^2}{E_{\rm dir}-\hbar\omega}$$

and

$$\alpha_{\text{ind}\,\ell}(\hbar\omega)=\alpha_{\text{absorption}\,\ell}(\hbar\omega)+\alpha_{\text{emission}\,\ell}(\hbar\omega)\ .$$

On the other hand, Dumke has calculated the shape of the absorption coefficient for direct transitions between an impurity level and an electronic band.[17] Prior to fitting experimental data, Dumke's expressions must be convoluted with a Lorentz function to take into account the broadening due to defects in the periodicity of the crystal.[18,19]

B. Analysis procedure

All of the absorption-coefficient spectra showed a nonvanishing plateau on the low-energy side (Figs. 1 and 2), which was attributed to reflectivity losses due to imperfections of the surface of the samples. To neglect this contribution, we have simply added a constant to the expressions for the absorption coefficient used in the analysis.

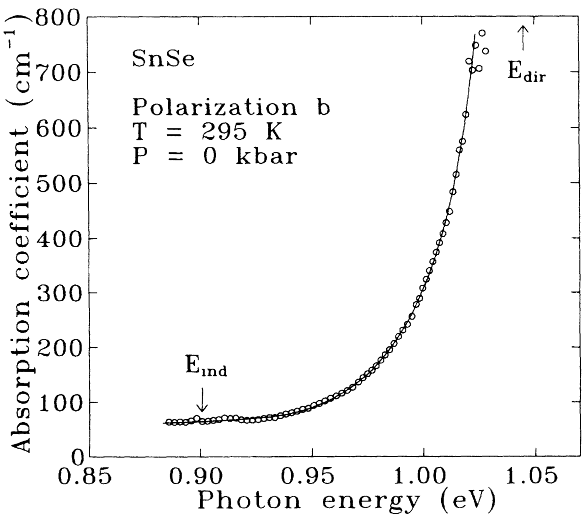

FIG. 1. Modeling of the absorption coefficient of SnSe in the **b** polarization in the indirect transition region. Experimental data, ○○○; Modeling with formula (1), solid curve.

In the **b** polarization, expression (1) fitted experimental data exactly, without allowing the evaluation of the energy of the phonon involved in the indirect transition, however. A typical value of 20 meV corresponding to values found by Raman measurements[20] was thus given to the phonon before modeling of the data was performed. With light polarized to the **a** axis, only the spectra obtained at room temperature or at high pressure could be analyzed as simply. At lower temperature, the presence of an additional absorption structure (hump) in this polarization prevented us from using the same procedure to

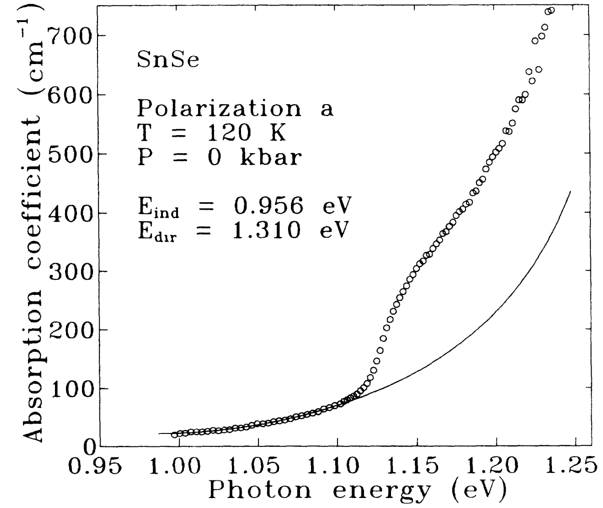

FIG. 2. Absorption coefficient of SnSe in the **a** polarization. Experimental data, ○○○. Modeling with formula (1), accounting for the presence of direct and indirect gaps only, without the impurity level, solid curve.

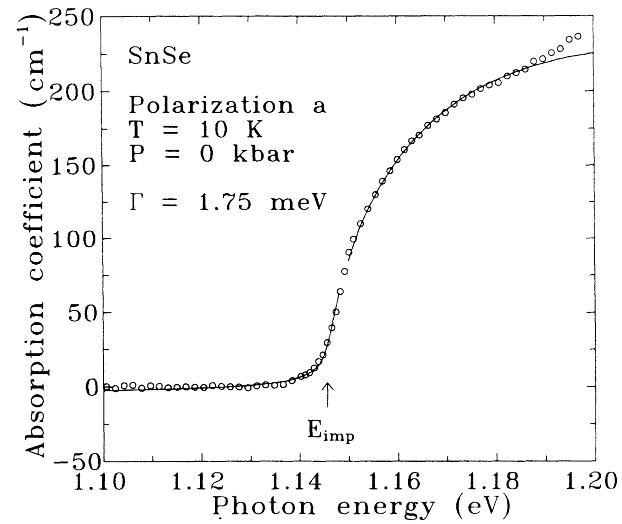

FIG. 3. Absorption structure in SnSe in the **a** polarization attributed to a direct transition involving an impurity level. Experimental data, ○○○. Modeling with formula (8) or (9) of Ref. 17 convoluted with a Lorentz function below 1.148 eV, solid curve. The threshold energy is named E_{imp}.

determine the transition energies. Instead, the following method was used.

(1) The direct band gap of SnSe was obtained by modeling the high-energy side of the absorption spectrum ($\alpha > 1000\ \text{cm}^{-1}$) with a curve convoluted with a Lorentz function:[18,19]

$$(\hbar\omega - E_{\text{dir}})^{1/2} \rightarrow \left[\frac{\Gamma}{2}\right]^{1/2} [x_p + (x_p^2+1)^{1/2}]^{1/2}\ ,$$

$$\text{with } x_p = \frac{\hbar\omega - E_{\text{dir}}}{\Gamma}\ . \tag{2}$$

The direct band gap of SnS could not be measured, owing to the low sensibility of the system for $\lambda < 750$ nm. Therefore, we used the value found in Ref. 1.

(2) The expression (1) was then fitted to the part of the spectrum preceding the hump, with the value for the direct band gap being fixed, so that we obtained the threshold for the indirect transition and the absorption curve attributed to indirect and direct interband transitions only, without the hump (Fig. 2).

(3) This absorption curve was subtracted from the experimental curve and the resulting one was then analyzed with expression (8) or (9) of Dumke,[17] convoluted with a Lorentz function (with broadening parameter Γ) near the threshold energy E_{imp} (Fig. 3). The convoluted part of the theoretical curve was equivalent to expression (2).

C. Results

The threshold energies for electronic transitions in SnS and SnSe in the **a** and **b** polarizations at $T = 295$ K and $P = 0$ kbar are given in Table I and II and are compared with values found in the literature. The location of these transitions in the Brillouin zone is given in Ref. 6 for SnSe.

The fact that an absorption structure shows a dependence of type (2) implies a three-dimensional behavior of the electrons. No transition involving a two-dimensional density of electronic states can give rise to such an absorption structure for parabolic band extrema.[21,22]

In addition to the model proposed by Dumke,[17] two models for indirect transitions could account for this type of hump: a transition to a bound excitonic level, involving phonons,[23] and a transition assisted by a collision with an isoelectronic impurity,[24,25] where the electron or the hole stays bound to the impurity. In each of these cases, however, the transition threshold should occur below the indirect gap, contrary to what is observed here. Moreover, in the case of transitions assisted by phonons, many humps should appear instead of only one. The possibility of a forbidden direct transition, mentioned in Ref. 7, has also been considered here, owing to the closeness of this transition threshold in the **a** polarization and the direct band gap in the **b** polarization for both crystals. However, the shape of the hump $[\alpha(\hbar\omega) \propto (\hbar\omega - E_t)^{1/2}]$ is markedly different from the theoretical one[22] for a direct forbidden transition $[\alpha(\hbar\omega \propto (\hbar\omega - E_t)^{3/2}]$. The same objection applies to the possibility of an indirect transition to another minimum of the conduction band.[7] These arguments have lead us to consider as most plausible the hypothesis of a direct transition involving an impurity level and an electronic band.

The activation energies of the impurity level, calculated with the experimental threshold values, can be compared to those found by Asanabe[26] by means of Hall-effect measurements on SnSe samples doped with antimony (Table III). Glow-discharge mass spectroscopy

TABLE I. Transition thresholds in SnS, as measured in the present work and found in the literature, at $T = 295$ K and $P = 0$ kbar.

		Thresholds (eV)	
Polarization	Transition	This work	Published
a	indirect	1.076±0.009	1.142[a]
a	impurity level	1.321±0.002	
a	direct		1.600[b]
b	indirect	1.049±0.008	1.095[a]
b	direct	1.296±0.003	1.300[b]

[a] Reference 8.

[b] Reference 1.

TABLE II. Transition thresholds in SnSe, as measured in the present work and found in the literature, at $T=295$ K and $P=0$ kbar.

Polarization	Transition	Thresholds (eV) This work	Thresholds (eV) Published
a	indirect	0.898±0.003	0.939[a]
a	indirect		0.910[b]
a	indirect		0.948[c]
a	indirect		0.932[d]
a	indirect		0.940[e]
a	impurity level	1.055±0.002	
a	direct	1.238±0.004	1.240[f]
a	direct		1.236[b]
b	indirect	0.903±0.002	0.898[a]
b	indirect		0.907[b]
b	indirect		0.902[c]
b	indirect		0.889[d]
b	indirect		0.891[e]
b	direct	1.047±0.005	1.050[f]
b	direct		1.051[b]

[a] Reference 9.
[b] Reference 6.
[c] Reference 10.
[d] Reference 11.
[e] Reference 12.
[f] Reference 1.

measurements have revealed the presence of many elements in our samples (Table IV). As the transition is observed with similar amplitudes in both compounds, it seems reasonable to assume that the impurity involved in the transition (if it is caused by the same element in both compounds) should be present with similar concentrations in SnS and SnSe. Aluminium, nitrogen, and chlorine fulfill this requirement, contrary to silicon, carbon, and oxygen. Iron and lead are also present but at lower concentrations. Finally, vacancies, whose concentrations are unknown to us, could play a role in this transition.

IV. PRESSURE DEPENDENCE OF THE TRANSITION ENERGIES

We have obtained the values of the direct and indirect band gaps by means of expression (1). The uncertainties on these threshold energies as a function of pressure restricted their modeling to straight lines (Fig. 4). Table V gives coefficients measured in this work and those for isoabsorption curves[1] at pressures below 6 kbar. The decrease of the transition energies with increasing pressure seems to be a standard behavior for layered and molecular crystals,[27] as opposed to crystals with zinc-blende or wurtzite structures.[28,29]

TABLE III. Activation energy of the impurity level observed in the **a** polarization, compared to the value found in doped SnSe.

Crystal	Impurity	Activation energy (meV)
SnSe	Al, N, Cl?	194±4 ($T=10$ K)
SnSe	Al, N, Cl?	183±6 ($T=295$ K)
SnS	Al, N, Cl?	280 ($T=295$ K)
SnSe	0.1% Sb	150[a] ($T=295$ K)

[a] Reference 26.

V. TEMPERATURE DEPENDENCE OF THE TRANSITION ENERGIES

A. Theory

At a temperature T_0, the implicit and explicit contributions to the temperature dependence of the transition thresholds can be distinguished if one knows the temper-

TABLE IV. Impurity concentrations found in our samples as measured by glow-discharge mass spectroscopy.

Impurity	Concentration (ppm atomic) SnSe	SnS
C	80	5
N	0.6	0.4
O	90	5
Na	3	0.3
Al	2	1
Si	900	2
S	3	
Cl	2	6
Fe	0.2	0.1
Te	7	0.3
Pb	0.03	0.03

TABLE V. Pressure and temperature dependence of the transition thresholds of SnS and SnSe. Implicit and explicit contributions to the temperature dependence and ratio θ of these two contributions. Electron-phonon coupling constants obtained by the modeling of experimental data with Schmid's expression and its derivative with respect to temperature. Average phonon coupled to the electrons.

Pol.	Trans.	$\frac{\partial E_t}{\partial P}$ (meV/kbar)	$\frac{dE_t}{dT}$ (ours)	$\frac{dE_t}{dT}$ (published)	Impl. Contr.	Expl. Contr.	θ	Coupling constant $G^2/\sqrt{M}$ (Schmid)	Coupling constant $G^2/\sqrt{M}$ (deriv.)	Coupling constant g $(m_v^* = m_c^* = 0.75m_e)$ (Schmid)	Coupling constant g $(m_v^* = m_c^* = 0.75m_e)$ (deriv.)	Phonon (meV)
			$(10^{-4}$ eV/K)	$(10^{-4}$ eV/K)	$(10^{-4}$ eV/K)	$(10^{-4}$ eV/K)						
						SnS						
a	indirect	−5.6(6)	−2.4(2)	−4.05[a]	0.64	−3.1	−0.21	0.18	0.23	0.39	0.45	20±10
a	impurity		−2.9(2)					0.22		0.44		17±2
a	direct	−8.3(6)										
b	indirect	−6.0(4)	−3.6(2)	−4.37[a]	0.69	−4.3	−0.16	0.35	0.44	0.56	0.62	33±9
b	direct	−7.3(9)	−5.63(7)		0.83	−6.5	−0.13	0.61	0.70	0.73	0.78	40±20
						SnSe						
a	indirect	−5.2(9)	−3.2(2)	−4.3[b] −3.7[c]	0.55	−3.8	−0.14	0.29	0.31	0.50	0.51	23±5
a	impurity		−4.0(1)					0.31		0.52		19±2
a	direct	−3.6(5)	−4.3(2)	−2.0[d] −4.4[c]	0.38	−4.7	−0.08	0.28	0.29	0.49	0.50	14±3
b	indirect	−8.9(5)	−2.9(2)	−4.3[b] −4.3[c]	0.94	−3.8	−0.25	0.17	0.21	0.39	0.41	11±3
b	direct	−11.2(4)	−4.3(3)	−4.0[e] −4.4[c]	1.19	−5.5	−0.22	0.35	0.41	0.55	0.58	20±4
b	Sns	−13.0[f]										
a	SnSe	−6.5[f]										
b	SnSe	−13.0[f]										

[a] Reference 8.
[b] Reference 11.
[c] Reference 6.
[d] Reference 7.
[e] Reference 4.
[f] Reference 1.

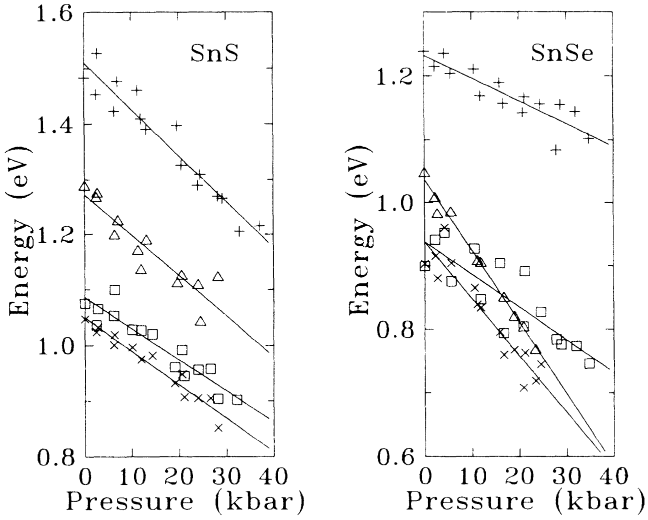

FIG. 4. Transition energies as a function of pressure at $T=295$ K. Indirect gap, **E**||**a**, □; direct gap, **E**||**a**, +; indirect gap, **E**||**b**, ×; direct gap, **E**||**b**, △. The solid lines give the linear fit to the data.

ature dependence of the transition energies E_t, the pressure dependence of these energies, the thermal expansion α_T, and the compressibility β of the crystal around T_0 in each case. Then[30]

$$\frac{dE_t}{dT}=\left[\frac{\partial E_t}{\partial T}\right]_V-\frac{\alpha_T}{\beta}\left[\frac{\partial E_t}{\partial P}\right]_{T_0}. \tag{3}$$

The first term on the right-hand side (RHS) of (3) gives the explicit contribution, while the second one gives the implicit contribution.

A few theoretical models have been developed to account for the temperature dependence of the transition energies of semiconductors.[31,32] They are based on self-energy or Debye-Waller corrections, or both. According to Schmid,[33] the interaction between electrons and nonpolar phonons polarized perpendicularly to the layers leads to a broadening Γ of the electronic energy levels and to a self-energy correction ΔE_t to the transition thresholds. His model neglects Debye-Waller corrections and interband coupling between electronic states.[31] The resulting expression for the Lorentz broadening parameter[33,34] contains the kinetic energy of the electron $\mathcal{E}$ and the electron-phonon coupling constant g (only the phonon branch ℓ is considered):

$$\Gamma=\begin{cases} g^2\sqrt{\hbar\Omega_\ell}\,n_\ell(\mathcal{E}+\hbar\Omega_\ell)^{1/2} & \text{for } \mathcal{E}<\hbar\Omega_\ell \\ \Gamma_0[n_\ell(a+1)+1] & \text{for } \mathcal{E}>\hbar\Omega_\ell\,, \end{cases} \tag{4}$$

where

$$\Gamma_0=g^2[\hbar\Omega_\ell(\mathcal{E}-\hbar\Omega_\ell)]^{1/2}$$

and

$$a=[(\mathcal{E}+\hbar\Omega_\ell)/(\mathcal{E}-\hbar\Omega_\ell)]^{1/2}\,.$$

In the case of an absorption structure caused by an electronic transition from the valence band to a conduction band, the total broadening parameter Γ comes from the broadening of the initial and final electronic states;[21] so that the coupling constant is the sum

$$g^2=g_v^2+g_c^2\,. \tag{5}$$

Similarly, the parameter experimentally accessible by the modeling of a threshold energy as a function of temperature [by expression (35) of Ref. 33], is a combination of the parameters belonging to the two bands:[21,35]

$$\frac{G^2}{\sqrt{M}}=\frac{g_v^2}{(m_v^*)^{1/2}}+\frac{g_c^2}{(m_c^*)^{1/2}}\,. \tag{6}$$

Through lack of knowledge of the energy of every phonon interacting with the electrons, the phonon energy appearing in expression (35) of Ref. 33 is assumed to be an average one.

B. Analysis procedure

With the help of expression (3) and of the parameters given in Table VI, we were able to separate the implicit and explicit contributions and evaluate their ratio θ:

$$\theta=\frac{\text{Effects of change of volume (implicit)}}{\text{Effects of interactions (explicit)}}=\frac{\dfrac{-\alpha_T}{\beta}\left[\dfrac{\partial E_t}{\partial P}\right]_{T_0}}{\left[\dfrac{\partial E_t}{\partial T}\right]_V}\,. \tag{7}$$

On the other hand, we have used three different methods to calculate the parameters of Schmid's model. The first one consisted in modeling the transition energies as a function of temperature, with the help of formula (35) of Ref. 33 (Fig. 5). The second one considered the derivative of this same formula with respect to temperature, at room temperature, and used the phonon energy obtained by the first method. Then the last method was to fit the Lorentz broadening parameter of the transition involving an impurity level with expression (4) (Fig. 6). The coupling constant (5) was obtained directly using this method. The effective masses m_v^* and m_c^* could be sub-

TABLE VI. Parameters used to calculate the contributions to the temperature dependence of the transition energies.

Crystal	Thermal expansion (α_T) (10^{-5}/K)	Compressibility (β) (10^{-3}/kbar)
SnS	2.17[a]	1.9±0.2[b]
SnSe	2.10[a]	1.99±0.02[c]

[a] Reference 36.

[b] Average of the compressibilities of GeS, GeSe, and SnSe (Ref. 37).

[c] Reference 37.

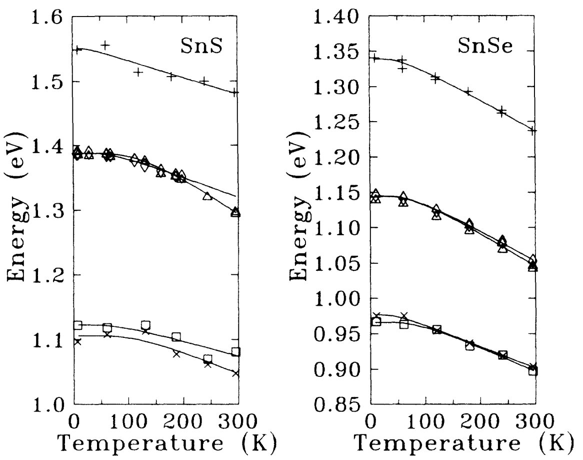

FIG. 5. Transition energies as a function of temperature at $P=0$ kbar. The formula (35) of Ref. 33 is used to model the data (solid curve). Indirect gap, $\mathbf{E}\|\mathbf{a}$, □; transition involving an impurity level, $\mathbf{E}\|\mathbf{a}$, ◇; direct gap, $\mathbf{E}\|\mathbf{a}$, +; indirect gap, $\mathbf{E}\|\mathbf{b}$, ×; direct gap, $\mathbf{E}\|\mathbf{b}$, △.

sequently evaluated by comparing this coupling constant to the one obtained by the first method [expression (6)]. This procedure has been used with SnSe only, the scatter in the values of Γ for the SnS being too large. It has then been assumed that the effective mass $M=0.75m_e$, found for the impurity transition in SnSe, was equal to m_v^* and m_c^*, and was the same for the bands involved in other transitions and for the bands in SnS. We used this effective mass to calculate the coupling constant g.

An advantage of the first and third methods was to use and to account for the data at all temperatures. They also allowed us to estimate the energy of an average phonon coupled to the electrons. On the other hand, they did not permit us to isolate the contribution of interactions at a fixed volume, which is the only one accounted for by Schmid's model. The second method's advantages and disadvantages were the opposite. The parameters obtained by the first two methods are given in Table V.

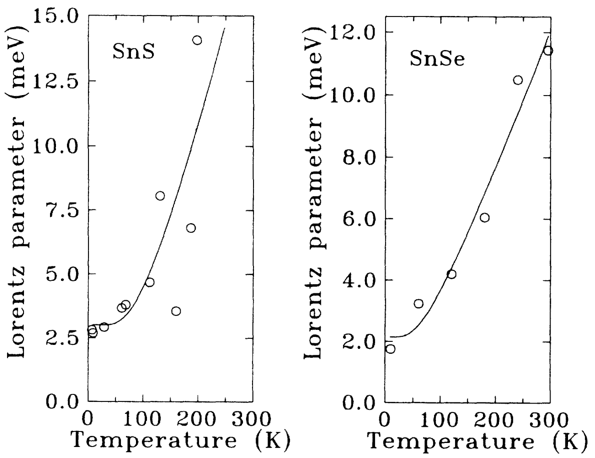

FIG. 6. Lorentz broadening parameter of the transition involving an impurity level ($\mathbf{E}\|\mathbf{a}$) as a function of temperature at $P=0$ kbar. The formula (4) (solid curve) is used to fit the experimental data (○○○).

A model giving the coupling between the electrons and the polar phonons of the crystal[33] has also been used to fit the experimental data. However, in order to account for the complete temperature dependence of the gaps, the coupling constants of this model had to be 20 times the value measured by infrared reflectivity on SnS.[38] Thus, the contribution coming from this coupling has been assumed to be negligible.

C. Results

Both contributions to the temperature dependence of the threshold energies are given in Table V. We can see that implicit and explicit contributions have opposite effects (θ is negative), the latter dominating and leading to negative temperature coefficients. This behavior is closely related to the pressure coefficient and, once again, seems to be the standard one for layered and molecular crystals.[27] For crystals with zinc-blende and wurtzite structures, the explicit and implicit contributions act in the same direction.[27]

The temperature coefficients found in other laboratories are quite different from ours (Table V). The values proposed in Ref. 6 for SnSe are based only on measurements at 95 and 295 K, however. Regarding the ones published for indirect transitions,[8,11] even the threshold values found there differ markedly from the ones we measured. In those works, the absorption-coefficient spectra were analyzed by means of a model that does not consider direct and indirect gaps simultaneously. The different analysis procedures, which give different threshold values, seem to influence the measured temperature dependence of the transition energies as well.

Table VII gives the energies of the phonons polarized perpendicularly to the layers, as measured by Raman spectroscopy.[20] The phonon energies obtained in the present work (Table V) are closer to the ones associated to the layer-breathing mode (at $\mathbf{k}=\mathbf{0}$). However, the large experimental uncertainties on the phonon energies and the fact that the dispersion curves for the phonons of these compounds are unknown make it difficult to choose a particular phonon as the main one interacting with the electrons.

The Schmid's coupling constants g obtained for various layered compounds[14,34,35,40] are close to the ones measured here for SnS and SnSe (Table V). This tends to confirm the validity of the present analysis. Consequently, the temperature dependence of the crystals SnS and

TABLE VII. Energy of the phonons polarized perpendicularly to the layers, as measured by Raman spectroscopy (Refs. 20 and 39).

Description	Phonon energy (meV) SnS	SnSe
Layer-waving mode	11.8	8.8
Layer-breathing mode	23.9	16.2

SnSe is mainly attributed to the coupling between electrons and nonpolar phonons.

VI. CONCLUSION

Dumke, Lorenz, and Pettit's expression for the absorption coefficient has allowed us to measure accurately the direct and indirect band gaps in SnS and SnSe compounds in the **a** and **b** polarizations. New values are proposed for the indirect band gaps at $T=295$ K, while the published values for the direct band gaps are confirmed (for SnS: $E_{\mathrm{ind}\,\mathbf{a}}=1.076$ eV, $E_{\mathrm{ind}\,\mathbf{b}}=1.049$ eV, and $E_{\mathrm{dir}\,\mathbf{b}}=1.296$ eV; and for SnSe: $E_{\mathrm{ind}\,\mathbf{a}}=0.898$ eV, $E_{\mathrm{ind}\,\mathbf{b}}=0.903$ eV, $E_{\mathrm{dir}\,\mathbf{a}}=1.238$ eV, and $E_{\mathrm{dir}\,\mathbf{b}}=1.047$ eV). In both crystals, a transition involving an impurity level is observed in the **a** polarization. The shape of this structure reveals the three-dimensional nature of the electronic properties of these layered compounds.

The measured pressure coefficients (in meV/kbar) for the various transitions are, for SnS: $dE_{\mathrm{ind}\,\mathbf{a}}/dP=-5.6$, $dE_{\mathrm{ind}\,\mathbf{b}}/dP=-6.0$, $dE_{\mathrm{dir}\,\mathbf{a}}/dP=-8.3$, and $dE_{\mathrm{dir}\,\mathbf{b}}/dP=-7.3$; and for SnSe: $dE_{\mathrm{ind}\,\mathbf{a}}/dP=-5.2$, $dE_{\mathrm{ind}\,\mathbf{b}}/dP=-8.9$, $dE_{\mathrm{dir}\,\mathbf{a}}/dP=-3.6$, and $dE_{\mathrm{dir}\,\mathbf{b}}/dP=-11.2$. In the temperature dependence of the transition energies, the effect of interactions is opposite to and much larger than the one due to the change of volume. The resulting temperature coefficients (in meV/K) are, for SnS: $dE_{\mathrm{ind}\,\mathbf{a}}/dT=-0.24$, $dE_{\mathrm{ind}\,\mathbf{b}}/dT=-0.36$, and $dE_{\mathrm{dir}\,\mathbf{b}}/dT=-0.563$; and for SnSe: $dE_{\mathrm{ind}\,\mathbf{a}}/dT=-0.32$, $dE_{\mathrm{ind}\,\mathbf{b}}/dT=-0.29$, $dE_{\mathrm{dir}\,\mathbf{a}}/dT=-0.43$, and $dE_{\mathrm{dir}\,\mathbf{b}}/dT=-0.43$. A coupling constant for the interaction between electrons and nonpolar phonons has been obtained for every transition, as well as the energy of a phonon polarized perpendicularly to the layers and interacting with the electrons.

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