Optical properties of InSb between 300 and 700 K. I. Temperature dependence of the energy gap

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We have determined the energy gap $E_g$ of InSb in the temperature range 300–700 K from infrared transmission experiments. The temperature dependence of the energy gap $E_g(T)$ is found to be accurately described by the empirical relation $E_g(T) (\text{meV}) = 235 - 0.27T^2/(T + 106)$. This observation extends the range of validity of this expression from 300 to 600 K, and this result may be of importance for use with modern finite-temperature first-principles band-structure calculations.

I. INTRODUCTION

Although InSb is among the most studied semiconductors, its high-temperature optical properties have only recently started to be investigated. In particular, the energies of the critical points of the InSb band structure have been measured with ellipsometric optical techniques. However, the magnitude of the fundamental gap at the $\Gamma$ point, $E_g$, has only been studied experimentally in the range 2–300 K (Refs. 2 and 3). In this paper we report infrared transmission experiments near the fundamental absorption edge for temperatures between 300 K and 670 K. The absorption coefficient $\alpha$ is extracted from the transmission experiments as a function of temperature and with these data the temperature dependence of the energy gap is obtained. These results are important for use with theoretical calculations of band structure at finite temperatures as can be done with modern techniques. A comparison with recent theoretical results of Zollner, Gopalan, and Cardona shows that the experimental temperature dependence of the gap is much weaker than the theoretical one. For instance, the theory predicts that the InSb band gap will become zero around 600 K, while experimentally a finite gap is found for all temperatures below 800 K. That is InSb remains a semiconductor up to the melting point (800 K).

II. EXPERIMENTAL DETAILS

Nominally undoped InSb samples with carrier concentration $1.0 \times 10^{14} \text{cm}^{-3}$ and mobility $5.6 \times 10^5 \text{cm}^2/\text{V sec}$ at 77 K were studied. Thin slices were cut from a crystal wafer, polished, and etched down on both sides to a desired thickness that was between 30 and 300 $\mu$m. The samples were placed in a sample room that was filled with high-purity helium gas to ensure homogeneous heating and to avoid oxidation of the sample. The ensemble was mounted in a furnace in the center of the sample room of a Fourier-transform spectrometer (Bruker IFS 113V) with which transmission measurements were performed in the energy range between 400 and 6000 cm$^{-1}$. The transmission coefficient of the sample was obtained by dividing the transmitted signal with a sample in the furnace by that of a reference spectrum, taken without a sample in the furnace. Since at higher temperatures due to free-carrier absorption, even for the thinnest samples, the signal intensity became too weak, data could be taken only up to 700 K.

The transmitted signal depends both on absorption and on reflection, therefore we eliminated the reflection coefficient of the air-InSb interface by comparing the results of two different samples of the same material but with different thicknesses $d_1$ and $d_2$, respectively. In that case the transmission ratio of these two samples is given by

$$\frac{T_{d1}}{T_{d2}} = \exp[-\alpha(d_1 - d_2)],$$

from which the absorption coefficient $\alpha$ can be obtained directly using the measured thicknesses.

III. EXPERIMENTAL RESULTS

In Fig. 1 we show the transmission data for the 40-$\mu$m sample as a function of energy and temperature. At 300 K a sharp increase in transmission is observed at 1350 cm$^{-1}$, showing the transparency of the sample for energies below the gap. For increasing temperatures this onset becomes less pronounced and moves to lower energies. At the same time the sample transmission for energies below the gap diminishes. This reduced transparen-

![Fig. 1. Transmission spectra as a function of energy at different temperatures. The symbol I indicates the position of the energy gap, obtained from the analysis of the absorption coefficient.](image-url)
cy is due to free-carrier absorption, which increases with temperature because of the increase in the carrier density.

In Fig. 2, we show the measured absorption coefficient $\alpha$ as a function of energy at different temperatures. They are extracted from the transmission spectra of three samples with different thicknesses. Using Eq. (1), the solid line is obtained for two samples of 40 and 260 $\mu$m and the dashed for samples of 60 and 260 $\mu$m. The agreement between these two lines at each temperature is quite satisfactory, and shows that reliable values of $\alpha$ as a function of temperature and energy are obtained. It can be seen that at high energies $\alpha$ increases rapidly with the energy of the incident photons due to the fundamental absorption around the energy gap. The onset of the increase in the absorption coefficient occurs at lower energies for increasing temperatures. This behavior directly reflects the decrease of the fundamental gap with increasing temperature. Limited by the sample thickness, the highest value of $\alpha$ in our measurements is less than 350 cm$^{-1}$.

IV. DISCUSSION

In an intrinsic semiconductor, neglecting interactions between particles, the absorption coefficient for direct-gap transition, as is the case of InSb ($k=0$), can be expressed as$^5$:

$$[\alpha h\omega]^{1/2} \equiv A (\hbar\omega - E_g)^{1/2} ,$$

where $\hbar\omega$ is the incident photon’s energy and $A$ is a constant. According to this equation, $\alpha$ increases abruptly from zero to a large value at an energy lower than $\hbar\omega = E_g$ and becomes weakly sensitive on the photon energies at higher energies. This absorption edge corresponds to the direct transition of electrons from the valence band to the conduction band. However, the experimentally observed absorption coefficient is affected on the low-energy side (inside the gap) by virtual absorption involving interactions with phonons, and on the high-energy side by the occupation of states in the valence and conduction band. In high-temperature measurements these two effects are particularly important due to the high phonon density and the high electron density. In order to determine the energy gap as a function of temperature we must therefore fit the measured absorption coefficient to calculations that account for these effects, using the band gap as a fit parameter.

The importance of phonon-mediated transitions can be directly seen from Fig. 2. At room temperature the InSb band gap has a value of 177 meV according to Fang et al.,$^2$ yet already at 160 meV $\alpha$ differs notably from zero, increasing from about 20 cm$^{-1}$ around 165 meV to 350 cm$^{-1}$ in a range of 20 meV.

1. Phonon broadening. This mechanism can simply be described as the following. For a direct semiconductor, one electron can be excited from the valence band to a virtual state below the conduction-band edge by absorption of a photon, and then be scattered into a real state of the conduction band by absorption of a phonon. This mechanism leads to an absorption tail below the energy gap. The variation of the absorption intensity with temperature follows the factor $(e^{\theta/T_1} - 1)^{-1}$, with the Debye temperature $\theta=290$ K, if we consider only long-wavelength optical phonons and neglect the energy difference between phonons of different optical modes. Dumke$^7$ developed a model for this process for direct semiconductors, which gives the following expression for $\alpha$:

$$\alpha = A' \frac{1}{E_g} \left[ \frac{\varphi}{(\varphi^2 - 1)^{1/2}} - 1 \right]$$

and

$$\varphi = \frac{2}{\alpha_v/\alpha_c} \frac{E_g - \hbar\omega}{\hbar\omega + k_B\theta - E_g} + 1,$$

where $A'$ is a constant and $\alpha_v/\alpha_c$ is the mass ratio between holes and electrons. $A'$ determines the amplitude of $\alpha_v/\alpha_c$ the curvature of the spectrum, and $E_g$ the position of the absorption edge. This model is limited in the energy range between $E_g - k_B\theta$ and $E_g$ since $\varphi$ must be larger than unity.

We consider that in our case the residual absorption below the energy gap is due primarily to the indirect transitions of electrons accompanied by absorption of an optical phonon, and ignore acoustical phonons or impurity-related effects. At high temperatures, the effect of acoustic phonons is negligible due to their low energies, while the impurity density is too low in our samples to be important. Using Dumke’s model,$^7$ we fit the spectra of $\alpha$ with the parameters $A'$ and $E_g$, taking $\alpha_v/\alpha_c=20$ which corresponds to the mass ratio at the band edge. In any case, Dumke’s studies have shown that the curvature of $\alpha$ is only weakly dependent on the precise value of the mass ratio.

In Fig. 3, we show four fitted curves of $\alpha$ as a function of energy together with the experimental results. The agreement between the two is satisfactory and from the fit we obtain the energy gap of InSb at each temperature, shown in Figs. 1 and 2.

2. Band-filling effects. In the transmission spectra of the sample of 40 $\mu$m, shown in Fig. 1, the position of the energy gap as obtained from the previous analysis of the absorption coefficient is indicated. This energy cuts the transmission edge to two parts: At the low-energy side,
the shape of the spectrum is due to the indirect transitions of electrons assisted by optical phonons, as discussed previously. At the high-energy side, the shape is due to direct transitions of electrons from the valence band to the conduction band. Due to the sample thickness no transmission can be observed at energies above the band edge at the lower temperatures because of the high value of the absorption coefficient. At higher temperatures, the number of carriers increases and at the highest temperatures the states near the band edge become filled. Therefore the absorption coefficient at energies slightly above the edge is reduced because of the lack of empty states, which is why these direct transitions are only observed in the spectrum of \( \alpha \) at 570 K and higher. In Fig. 4 we show the shape of \( \alpha \) for the below-band-gap absorption (the dashed line in the figure, taken at 450 K) and that of the above-band-gap absorption (the solid line, taken at 570 K). In these high-temperature data the expression for \( \alpha \) must take into account the occupancy.

Considering the distribution of the free carriers in both bands, the absorption coefficient for this case can be expressed as

$$\alpha(k) = \alpha_0 [1 - f_c(k)].$$

(5)

\( \alpha_0 \) is the absorption coefficient for small carrier concentration and is given by Eq. (2), \( f_c(k) \) is the state density of electrons at the wave vector \( k \), and \( f_c(k) \) is the Fermi distribution function. Due to the high mass and the high density of states for the holes, we may neglect the emptying of the hole states; near the top of the valence band the hole states are occupied. Taking the zero of the energy scale at the bottom of the conduction-band edge.

$$f_c(k) = \frac{1}{\exp[(E - E_F)/k_B T] + 1},$$

(6)

where \( E_F \) is the Fermi energy of InSb.

Using Eqs. (2), (5), and (6), we can fit the spectrum of \( \alpha \) at 570 K with the parameters \( A, E_g \), and \( E_F \), and the result is satisfactory, as can be seen from Fig. 4. We obtain \( E_g = 92 \) meV and a positive value for \( E_F = 70 \) meV, which is because the Fermi level of intrinsic InSb at high temperatures is above the bottom of the conduction band. The fact that intrinsic InSb at high temperatures becomes degenerate is due to the considerable difference between the hole mass and the electron mass (\( m_h \geq 10m_e \)). As will be shown in the following paper, the Fermi level and its temperature dependence, which is determined from magneto-optical measurements, is fully consistent with the interband experiment results reported here.

V. TEMPERATURE DEPENDENCE OF THE GAP OF INSB

It is well known that the energy gap of semiconductors decreases with increasing temperature. One contribution to this effect comes from the thermal dilatation of the lattice, which reduces the overlap between of electronic wave function of neighboring atoms. The second contri-
TABLE I. List of calculated fitting parameters for the temperature dependence of the gap of InSb
(where IR denotes infrared, PL denotes photoluminescence, and FT denotes Fourier transform).

<table>
<thead>
<tr>
<th>( E_g ) (meV)</th>
<th>( a ) (meV/K)</th>
<th>( b ) (K)</th>
<th>Experimental technique</th>
<th>Temperature range investigated (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>235</td>
<td>0.270</td>
<td>106</td>
<td>IR-PL</td>
<td>10–300</td>
<td>2</td>
</tr>
<tr>
<td>235</td>
<td>0.299</td>
<td>140</td>
<td>FT-PL</td>
<td>5.1–8.1</td>
<td>11</td>
</tr>
<tr>
<td>236</td>
<td>0.299</td>
<td>140</td>
<td>piezorefection</td>
<td>77–300</td>
<td>12</td>
</tr>
<tr>
<td>235</td>
<td>0.6</td>
<td>500</td>
<td>resonant two-photon</td>
<td>2–210</td>
<td>3</td>
</tr>
</tbody>
</table>

The contribution to the energy dependence of the gap comes from electron-phonon interaction (Debye-Waller term). Both contributions are about equally important; the first one can be easily evaluated from the measured pressure dependence of the gap and the second one needs to be calculated using more detailed theoretical models. In particular, this second term is responsible for the difficulties in calculating accurately the temperature dependence of the gap.\(^9\)

Since it is not possible to compare directly with an explicit theoretical formula it is customary to describe the temperature dependence of the energy gap with an empirical formula according to Varshni:\(^10\)

\[
E_g = E_{g0} + aT^2/(T + b) ,
\]

where \( E_{g0} \) is the energy gap at 0 K and \( a \) and \( b \) are two empirical parameters. Fang et al.\(^2\) summarized the main experimental results at low temperatures for the values of the energy gap of InSb, which are shown in Table I. It can be seen from this table that the discrepancy between different groups concerns mainly the empirical parameters \( a \) and \( b \), whereas the same value of the energy gap at 0 K is found.

Our results on the energy gap as a function of temperature are shown in Fig. 5 by the open circles. In order to calculate two empirical parameters \( a \) and \( b \), we have used 235 meV as \( E_{g0} \). We find that our high-temperature data can be described with the same values as those obtained by Fang et al.\(^2\) for low-temperature data. Their results are also shown in Fig. 5 by the closed circles. The dashed line represents the relation

\[
E_g(T) = 235 - 0.27T^2/T + 106
\]

and is found to accurately describe the experiments between 10 and 650 K.

Table I compares three different sets of values for the experimentally determined parameters \( a \) and \( b \) to describe the temperature dependence of the band gap. Although the values of these coefficients are quite different, the prediction of the temperature dependence below room temperature is rather similar. For instance, at 300 K the predicted values of the energy gap for the three parameter sets are the same within 4%. At higher temperatures differences become more apparent. In particular, the parameter set of Auvergne et al.\(^11\) predicts a much faster decrease of the gap with measuring temperature than the other models. For instance, the predicted temperature where the predicted gap is zero is 965 K for our parameters, 907 K for the parameter set of Rowell,\(^11\) and 680 K for that of Auvergne. These latter values are in clear contradiction with our data since we still observe a finite transmission at 670 K (see Fig. 1).

Many theoretical studies have been performed in the past (Ref. 6 and references cited therein). Recently, Zollner, Gopalan, and Cardona\(^4\) have calculated the energy gaps of InSb, InP, InAs, and GaSb up to 600 K. Their calculated result for InSb, represented in Fig. 5 by the solid line describes correctly the trend of the variation of the gap with temperature, but quantitatively there is, especially at high temperatures, an important discrepancy between their results and our experiments. In particular, their calculation predicts a zero value for the gap slightly above 600 K, whereas we measure a value of 90 meV at that temperature. Using Eq. (7) a zero gap would be predicted at 965 K, which is much higher than the melting point of InSb (800 K). At the melting point a gap of 44 meV is predicted using Eq. (7).

VI. CONCLUSION

In conclusion, we have measured the transmission of intrinsic InSb near the fundamental absorption edge from 300 to 700 K. Two contributions to the absorption coefficient are observed: indirect transitions below the energy gap, accompanied by absorption of optical phonons and the direct transitions above the gap, influenced by the occupancy of states near the band edge by free carriers at high temperatures. We find that the temperature dependence of the energy gap of InSb from 0 up to 700 K can be accurately expressed by the empirical relation shown in Eq. (8). With these data the range of validity of this equation has been extended from 300 to 700 K, which is close to the melting point of InSb. We believe that these results may be of importance for testing ab initio band-structure calculations at finite temperatures.

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