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THE TEMPERATURE DEPENDENCE OF THE BAND GAPS IN InP, InAs, InSb, AND GaSb

Stefan Zollner, Sudha Gopalan, and Manuel Cardona

Max-Planck-Institut für Festkörperforschung,
Heisenbergstrasse 1, D-7000 Stuttgart 80,
Federal Republic of Germany

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We calculate the dependence of the direct band gaps E_0 on temperature in the narrow-gap materials InP, InAs, InSb, and GaSb. Our calculation is based on the Allen-Heine approach and includes two effects: (i) thermal expansion and (ii) electron-phonon interaction. The latter when expanded in perturbation theory up to second order in the atomic displacements includes two terms: Debye-Waller and self-energy (or Fan-) terms. The results obtained by including all these terms within the rigid-pseudoion model compare reasonably well with available experimental results.

InP, InAs, InSb, and GaSb are four narrow-gap semiconductors with great potential for use in infrared lasers or other electro-optical devices. [1] Therefore, the knowledge of the band structures of these materials along with their temperature dependence is of technological interest. In recent years, some experimental work has been performed to investigate the magnitude of E_0, the direct band gap at the Γ-point, as a function of temperature in these materials. [1-7] In this work, we describe briefly the theory of the temperature dependence of band gaps and compare the results obtained for E_0 from such a calculation with those found experimentally for the narrow-gap semiconductors listed above. Our work gains additional importance by the fact that the same electron-phonon interactions that cause the band gap changes also the determine the high-field transport properties of solids.

The process of finding a theoretical description for the temperature dependence of the band structure has been rather long and cumbersome. [8-13] The fundamental technique was formulated by Allen and Heine [14] and includes two contributions to the temperature dependence of the gaps: (i) The effect of thermal expansion is a trivial increase of the lattice constant with increasing temperature thereby shrinking (sometimes widening) the band gaps. This effect accounts only for at most 30% of the observed shifts and sometimes (like in the case of the indirect gap of silicon) even yields the wrong sign. (ii) The renormalization of the electronic energies due to electron-phonon interaction gives rise to two terms: The Debye-Waller (DW) term can be calculated rather easily and gives the dominant contribution. [15] The self-energy (or Fan-term), though smaller, is often opposite in sign to the DW term. Therefore, an approach which neglects the self energy may overestimate the band gap shrinkage. [15]

The Allen-Heine formalism treats both the DW and self-energy terms on an equal footing. [14] They are obtained upon expansion of the electron-phonon interaction in perburbation theory and retaining terms up to second order in phonon amplitudes. The DW term corresponds to a two-phonon process, whereas the self-energy term is an iterated one-phonon process. This method has been used successfully to describe the lowering of the direct gaps with increasing temperature in Si, Ge, [16,17] and GaAs [18]. The numerical procedure is discussed in detail in Ref. [18]. We have verified that the "acoustic sum rule" used to evaluate the self energy term (see Ref. [16]) is also valid for compounds consisting of atoms with different masses. We use an empirical local pseudopotential band structure for InP, InAs, InSb, and GaSb with the form factors suggested previously [19] for InP and from Cohen and Bergstresser [20] for the other materials. Details of the interpolation of the pseudopotential form factors and their extrapolation [21] to $\vec{q}=0$ have a negligible effect on the magnitude of the shifts, but the form factors from Ref. [22] clearly overestimate the strength of the electron-phonon interaction in InSb. The phonon states were calculated with the 10-parameter valence overlap shell model [23,24]. The summation over all the phonon wave vectors $\vec{q}$ in the Brillouin zone (BZ), necessary to include all possible scattering channels, was performed with the tetrahedron method using a mesh of 89 $\vec{k}$-points which spans over 228 tetrahedra in an irreducible wedge of the BZ. Increasing the number of $\vec{k}$-points in the mesh to 505 changed the energy shifts by less than 2 meV for InP. The denominators in the expressions of the DW and self energy terms contain energy differences $\Delta E = E_{n\vec{k}} - E_{n',\vec{k}+\vec{q}}$, where $n\vec{k}$ are the initial and $n', \vec{k}+\vec{q}$ the intermediate electron states the carriers scatter into via phonon absorption or emission. We attached a Lorentzian broadening of 0.02 Ry to each such denominator in order to avoid numerical instabilities during integration. This also endows each of the electronic states with an imaginary self energy corresponding to 0.01 Ry, which is roughly what one obtains from the calculations of the broadenings or ultrafast relaxation of carriers at different $\vec{k}$-points. [25] The thermal

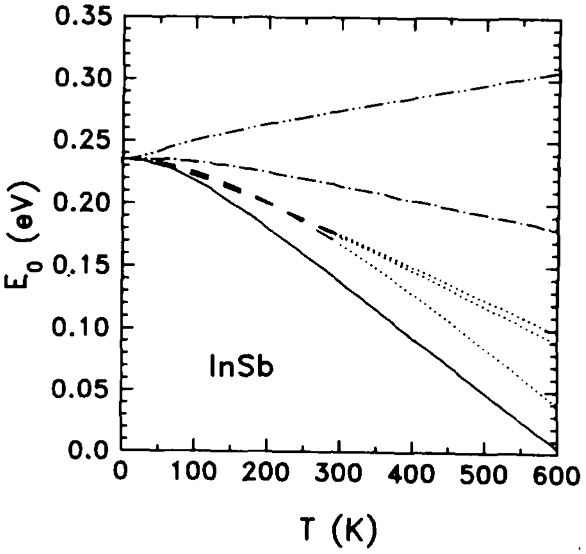

Fig. 1. Temperature dependence of the direct band gap E_0 of InSb. The dashed lines show the data of Refs. [1,2,5], measured between 0 and 300 K. The dotted lines extrapolate the experimental results to 600 K. The solid line displays the calculated shifts, including thermal expansion, Debye-Waller and self-energy term. For comparison, the contributions of thermal expansion (dashed-dotted) and self energy term (dashed-double dotted) alone are also given.

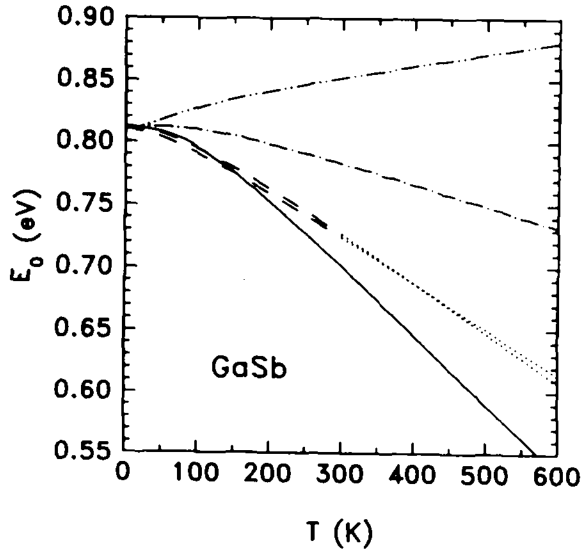

Fig. 2. As Fig. 1, but for GaSb with the experimental results from Refs. [1,4].

expansion effects were obtained easily using the thermal expansion coefficients, bulk moduli, and pressure coefficients taken from Refs. [26-28] The calculations were performed on a MicroVAX II minicomputer and used about ten hours of CPU time for each material.

In order to reduce the computational effort, the shifts were calculated for bands without spin-orbit interaction, which could change the size of the energy denominators mentioned above slightly. In order to study this effect we calculated these denominators with and without spin-orbit interaction for InAs, but obtained the matrix elements of the electron-phonon interaction from the unperturbed wave functions. We found that the shifts between 0 and 600 K were smaller when spin-orbit interaction was taken into account (as could have been expected), but only by about 10 meV, mainly due to a smaller self energy at the top of the valence band. The effects of spin-splittings on the Debye-Waller term (which is purely of orbital origin and can be calculated without energy denominators [15]) are smaller. In contrast, we have shown previously [25] that spin-orbit contributions to the temperature dependence of the broadenings of critical points can be significant.

We show our results in Figs. 1-4 in comparison with experiments. Figure 1 displays the direct gap E_0 in InSb as a function of temperature. The dashed lines are the results of different experiments [1,2,5] performed between 0 and 300 K. The dotted lines extrapolate the experimental results to 600 K. The dashed-dotted line shows the influence of thermal expansion only, which accounts for 20-30% of the observed shift. The dashed-double dotted line gives the self energy contribution, which leads to a band gap widening with increasing temperature and partially cancels the dominant Debye-Waller-term (not explicitly shown in Fig. 1). The total calculated temperature dependence of E_0, including all three terms, is represented by the solid line. Our theory overestimates the band gap shrinkage between 0 K and 300 K by about 40% and predicts InSb to be a semimetal for temperatures above 600 K. (The melting point of InSb is 800 K, see Ref. [26].) We stress that there were no adjustable parameters used in this calculation. Figures 2 and 3 show the results of our calculations for GaSb and InAs (solid lines). It can be seen that the agreement with the data of Refs. [1,4] is reasonable for GaSb, whereas the deviation from the experiments [1,2,29,30] for InAs is larger, possibly due to a numerical problem with the evaluation of the self

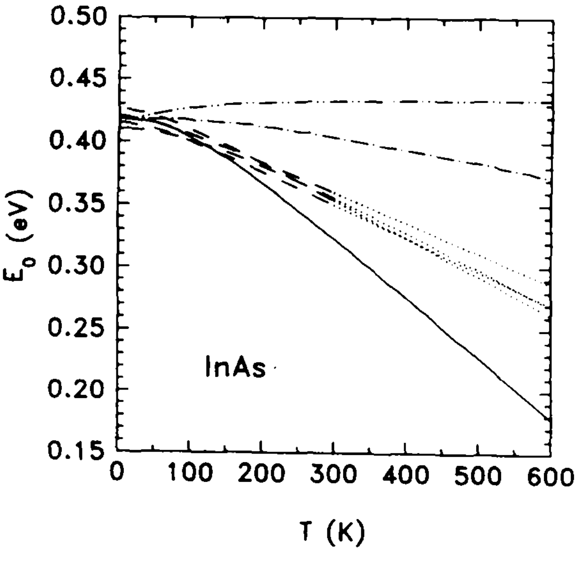

Fig. 3. As Fig. 1, but for InAs with the experimental results from Refs. [1,2,29,30].

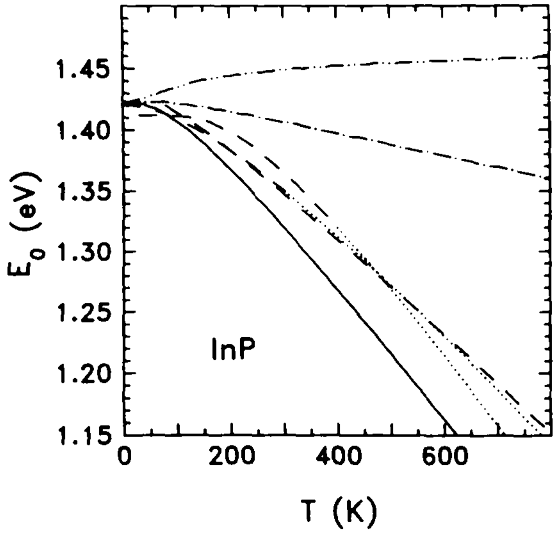

Fig. 4. As Fig. 1, but for InP with the experimental results from Refs. [29,6,7].

energy in the conduction band for the interaction with the transverse acoustic phonon at L. The difference between our calculated shifts for InP (solid line in Fig. 4) and the accurate photoreflectance results of Ref. [7] (dashed) is also reasonable.

The agreement between theory and experiments is not as good for the compounds investigated in this study as that obtained for the temperature and isotope shifts of gaps of lighter materials like diamond, [31] silicon, [16,17] and GaAs. [18] It is possible that the rigid-ion model becomes inaccurate for compounds with heavy atoms. This could be checked by calculating the electron-phonon matrix elements at high-symmetry points using *ab initio* electronic structures in conjunction with the frozen-phonon technique, [32-34] since such an approach would recalculate the charge densities and ionic potentials for the deformed crystal. The frozen-phonon technique calculates the electron-matrix elements from differences of crystal potentials rather than from a Taylor expansion [35] involving the derivative of the potential.

In conclusion, we have calculated the temperature dependence of the direct band gap in the narrow-gap compounds InP, InAs, InSb, and GaSb using the rigid pseudo-ion method. Our theory, when compared to experimental results, overestimates the shifts consistently by about 20–30%, possibly because of the use of interpolated empirical pseudopotentials or because of fundamental problems with the rigid-ion model for heavy materials. Other sources of uncertainties, like numerical problems with the Brillouin-zone integration necessary to calculate the self energy due to deformation-potential electron-phonon interaction or the influence of the spin-orbit interaction, were shown to have negligible effects.

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