Temperature dependence of transverse acoustic phonons in semiconductors

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The temperature dependence of TA phonons due to (i) electron-phonon interaction, (ii) lattice expansion, and (iii) phonon-phonon interaction is estimated using the simple dielectric model of any tetrahedral semiconductor. It is found that the phonon-phonon interaction has the greatest effect. For the case of Ge near its melting point the estimate is in agreement with recent neutron-scattering measurements of Hennion and Schott.

An understanding of the temperature dependence of phonon modes is useful for the interpretation of elastic and plastic deformation and of light scattering phenomena[1] in semiconductors at high temperature. It has even been proposed that an instability of zone boundary TA phonons is responsible for normal thermal melting of Si and similar crystals.[2] However, recent neutron-scattering measurements of TA-phonon dispersion in Ge to its melting point[3] by Hennion and Schott show only a modest ($\approx 11\%$) decrease of $\omega_{TA}(q,T)$ as temperature $T \rightarrow 1210$ K, its melting point. The various $d\omega_{TA}(q)/dT$'s were sensibly linear in T. Moreover, this percentage decrease is sensibly the same for all q along both the [111] and [100] axes; no evidence of the onset of a phonon instability at the (111) zone boundary, that is predicted[4] by Biswas and Ambegaokar for the case of excited electron densities $N \gtrsim 9\times 10^{21}$ cm^{-3}, was found. The last point is not an indication of an error on the part of Biswas and Ambegaokar because, contrary to the proposal[2] of Combescot and Bok, N is only about 2×10^{19} cm^{-3} for Ge at its melting point.[5,6]

Because the observed variation of phonon angular frequency, $\omega(q,T)$, with T is insensitive to the direction of q and proportional to $\omega(q,\ T=0)$, it is appropriate to look for a simple theory of this effect that neglects the sophistication and avoids the difficulty of calculating wave functions, evaluating many matrix elements, summing over states, and so forth. Such a simple model is the dielectric two-band model[7-9] for an arbitrary tetahedral semiconductor, which was introduced by Phillips and Van Vechten. Indeed, the elements necessary for this estimate were developed some time ago for a study of the temperature dependence of band gaps[10,11] and of the higher-order elastic constants.[12]

ω_{TA} may be expected to decrease due to three effects: (i) the excitation of electrons across the fundamental gap softens[10,11] the bond bending force constant of the Keating-Martin-Weber formulation of the phonon dispersion;[13-15] (ii) thermal expansion will cause a further decrease in the bond bending force constant, which will be approximated by the bond-length dependence, $d\omega_{TA}/dr$, deduced from hydrostatic pressure measurements;[12] and (iii) the interaction among phonons will affect ω_{TA} in a manner that will be estimated below.

Effect (i), the electron-phonon interaction, was treated by Heine and Van Vechten who give [Eq. (11) of Ref. 10]

$$\omega_{TA}(q,n_p)=\omega_{TA}(q,0)[1-n_p f_{cv}\epsilon_0\epsilon_0^*/(\epsilon_0^*-\epsilon_0)4N_A]\ , \qquad (1)$$

where n_p is the density of excited electron-hole pairs, ϵ_0 is the optical dielectric constant of the semiconductor when $T=0$ K and $n_p=0$, $\epsilon_0^*=24$ is a critical value of ϵ_0 set just above that of α-Sn (which is only marginally stable in the diamond structure), N_A is the density of atoms (so $4N_A$ is the density of valence electrons), and f_{cv} is the fractional change in bond charge density per electron-hole pair excited for the particular interband transition in question. (f_{cv} is about 0.85 for thermal excitation across the fundamental gap of common semiconductors.) Equation (1) was shown to give a good account of the temperature dependence of the fundamental band gap[10] and several higher interband gaps[11] for Si, Ge, and some III-V semiconductors. For both Si and Ge, Eq. (1) implies $\omega_{TA}(q)=0$ for all q (by construction) if $n_p=8\times 10^{21}$ cm^{-3}. Thus, the discrepancy between this simple formula and the more sophisticated calculation of Biswas and Ambegaokar, who found a q dependent critical n_p that ranges from 9 to about 30×10^{21} cm^{-3}, is not major. As the intrinsic value is $n_p=2\times 10^{19}$ cm^{-3} at the melting point of Ge and Si (and several other semiconductors),[5,6] the electronic effect acting alone would be expected to reduce ω_{TA} by only 0.25% at the melting point. Of course, the variation of this effect is not linear but that would not be noticed because it is small and indeed smaller than the effect of thermal expansion.

For effect (ii), that of the variation of lattice constant due to thermal expansion (less than 1% at the melting point[16,17]), will be treated using data derived for hydrostatic pressure. Reference 12, Eq. (18) gives the logarithmic derivative of the bond bending force constant,[13-15] β, as

$$(r/\beta)\partial\beta/\partial r=-3.5\ . \qquad (2)$$

Because ω_{TA} is roughly proportional to $\beta^{1/2}$, this implies a logarithmic derivative of -1.75 for ω_{TA}. If the thermal expansion to the melting point were as much as 1%, this would imply a decrease due to the thermal expansion of 1.75%. Thus, the sum of effects (i) and (ii) is estimated to be no more than a decrease of 2% in ω_{TA}, which is rather less than the $\sim 11\%$ decrease observed by Hennion and Schott. Again the variation of the expansion effect is calculated to be faster than linear, but this would not be evident in data dominated by a larger effect, i.e., (iii).

To estimate (iii), the effect of phonon-phonon interaction, note that Ref. 12 related β to ΔE_m [Eq. (8) with definition (3)], where ΔE_m is the internal energy of the covalently bonded tetrahedral crystal relative to a jellium model of a metallic phase that approximates the molten phase. ΔE_m is reduced as sensible heat is added to raise T. In the harmon-

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ic approximation, half this sensible heat is kinetic energy due to the thermal motion of the atoms and half is potential energy due to the distortion of the bonds. Thus, it seems that ΔE_m should be reduced by half the sensible heat in the sample. For Si, the sensible heat is 40%′of the total energy required to heat the sample from room temperature to the melting point and melt it; 60% of the total is the latent heat of melting.[18] For Ge, the compilation of data[19] by Neuberger indicates the same proportions. Therefore, one estimates that β is reduced by 20% due to interaction with all the phonons thermally excited at the melting points of either Si or Ge. This would imply a 10% reduction of ω_{TA}. Thus, the sum of effects (i), (ii), and (iii) would be between 10% and 12% as compared with $\sim 11\%$ found by neutron scattering. As the heat capacity is essentially independent of T at high temperatures, the largest term in the total thermal effect upon ω_{TA} would imply a linear variation of β with T and a $T^{1/2}$ variation for ω_{TA}. However, the difference between this and a linear variation of ω_{TA} would be difficult to detect for such a small range.

From the linewidths in their neutron scattering data Hennion and Schott deduced the zone boundary TA phonon lifetimes at the melting point of Ge to be 10 ps. This value is compatible with the thermal and electrical conductivity data[5] of Glassbreener and Slack and with their simple formula to deduce phonon lifetimes therefrom. They give for the lifetime due to Umklapp scattering, τ_U,

$$\tau_U^{-1} = B_U \omega^2 T \quad , \tag{3}$$

where

$$B_U \approx (h\gamma^2/2\pi M \Theta v^2)\exp(-\Theta/3T) \quad . \tag{4}$$

γ is Grüneisen's constant, which they find to be $\gamma = 2$, M the average mass of a single host atom, Θ the Debye temperature, and v the averaged sound velocity. This umklapp scattering was argued to be the dominant factor near the melting point; other effects such as electron-phonon scattering could only reduce the observed net τ, which is related to the various scattering factors as

$$1/\tau = 1/\tau_U + 1/\tau_{e\text{-ph}} + 1/\tau_I + \cdots \quad , \tag{5}$$

where $\tau_{e\text{-ph}}$ is the lifetime that would result from electron-phonon scattering alone, τ_I is that due to isotope scattering alone, etc. For Ge at 1210 K with $\Theta = 354$ K,[19] $\omega = 2\pi \times 2$ THz at the (100) zone boundary,[3] and $v = 4.5 \times 10^5$ cm/s gives $\tau_U = 11.9$ ps; as Hennion and Schott measure the net lifetime $\tau = 10$ ps, none of the other scattering times can be as short as 10^{-11} s, which is consistent with the analysis and conductivity data of Glassbrenner and Slack. For Si at 1685 K with[5] $\Theta = 674$ K, $v = 6.4 \times 10^5$ cm/s, and with $\omega = 2\pi \times 4$ THz at the (100) zone boundary[14] we have $\tau_U + 3.3$ ps.

As these simple models work well for both Si and Ge and for data on both thermal and electrical conductivity and for data on neutron scattering, there seems to be reason to expect they will serve for similar data on other tetrahedral semiconductors.

Note added in proof. Professor Schott informs the author that his initial data on Si near its melting point are also close to these estimates.

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