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DIELECTRIC FUNCTION AND PHONON SPECTRUM OF GREY TIN

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The dielectric function of α-Sn has been evaluated from a pseudopotential calculation of the valence electron wavefunctions and energy bands. The result is used, together with an approximate method of calculating the inverse of the dielectric function matrix, to calculate the phonon dispersion curves. Fairly good overall agreement with the experimental dispersion curves has been obtained.

1. INTRODUCTION

A MICROSCOPIC calculation of the phonon spectrum of a covalently bonded semiconductor involves a careful evaluation of the dielectric screening by the valence electrons. Recently, first principle calculations of the diagonal part of the dielectric function matrix $\epsilon(\mathbf{Q},\mathbf{Q})$ have become available for many of the covalently bonded semiconductors,[1] based on pseudopotential calculations of the valence electron wavefunctions and energy levels. In addition, a facorization *ansatz* for $\epsilon(\mathbf{Q},\mathbf{Q})$ has been developed[2–4] to generate from $\epsilon(\mathbf{Q},\mathbf{Q})$ an analytic expression for $\epsilon^{-1}(\mathbf{Q},\mathbf{Q}')$ and the method has been used to calculate the phonon spectra of silicon and germanium.[2–4] We present here a combined calculation of $\epsilon(\mathbf{Q},\mathbf{Q})$ for α-Sn and its phonon spectrum using similar methods. In these calculations, we have neglected effects due to spin–orbit interaction and have used a local pseudopotential to represent the ion-valence electron interaction.

An interesting point arises in connection with the fact that α-Sn is technically a zero-direct gap semiconductor[5] owing to the fact that the conduction and valence bands are degenerate at Γ. In the absence of free carriers, it may be shown[6] that $\epsilon(\mathbf{Q},\mathbf{Q})$ diverges as $1/Q$ as $\mathbf{Q} \to 0$.

However, Sherrington[7] has shown that for values of the reduced wavevector $q > 2\mu^* c$ (where μ^* is the reduced mass of the electrons in the touching bands, and c is the sound velocity), $\epsilon(\mathbf{Q},\mathbf{Q}')$ has the analytic behavior characteristic of ordinary insulators.[8,9] For α-Sn, $2\mu^* c \sim 10^3\,\mathrm{cm}^{-1}$. Further, for typical carrier concentrations of $\sim 10^{14}\,\mathrm{cm}^{-3}$, free carrier screening will possibly affect the lattice modes only for wavevectors $\lesssim 10^6\ \mathrm{cm}^{-1}$, the magnitude of the Thomas–Fermi wavevectors of the free carriers. Hence for discussing the portion of the phonon spectrum accessible to neutron experiments, we may neglect

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the zero-gap and free-carrier effects, and assume the validity of the usual acoustic sum-rule, which ensures linear acoustic behavior at low q.[8–10]

2. THE DIELECTRIC FUNCTION

We follow here the approach of references 1, 11 and and 12;

$$\epsilon(\mathbf{Q},\mathbf{Q}) = 1 + \frac{8\pi e^2}{Q^2}\frac{2}{(2\pi)^3}\sum_{k,v,c}\frac{|\langle \mathbf{k}+\mathbf{Q},v|\mathbf{k},c\rangle|^2(\Delta k)^3}{E_c(\mathbf{k}) - E_v(\mathbf{k}+\mathbf{Q})}$$

where the summation is over cubes of volume $(\Delta k)^3$ in the first Brillouin zone, with truncations at the boundaries. The indicies v, c span the top four valence and bottom 11 conduction bands. The energy eigenvalues and eigenvectors are calculated using the empirical pseudopotential method[13] and the pseudopotential form factors are those of reference 14. Spin–orbit effects are neglected. The eigenvalues and eigenvectors are computed at 3360 points in the first Brillouin zone. The coordinates of the grid of calculated points are given by $\frac{1}{16}(2s+1, 2m+1, 2n+1)$ in units of $2\pi/a$, where s, m and n are integers.

The results for $\epsilon(Q,Q)$ calculated along the ΓX, ΓL and ΓK directions are given in Fig. 1.

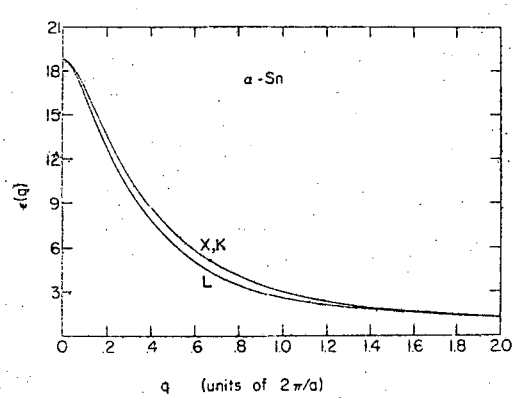

FIG. 1. The RPA dielectric function $\epsilon(\mathbf{Q},\mathbf{Q})$ for α-Sn calculated along the principal symmetry directions. The curve marked X, K corresponds to $\mathbf{Q}$ along ΓX and ΓK, and the curve marked L to $\mathbf{Q}$ along ΓL.

3. THE PHONON SPECTRUM

The microscopic expression for the dynamical matrix may be written

$$D_{\alpha\beta}(kk'|\mathbf{q}) = (M_k M_{k'})^{-\frac{1}{2}}[Z_k Z_{k'} C_{\alpha\beta}(kk'|\mathbf{q}) + \tilde{E}_{\alpha\beta}(kk'|\mathbf{q}) - \delta_{kk'}\lim_{\mathbf{q}\to 0}\sum_{k''}\{Z_k Z_{k''} C_{\alpha\beta}(kk''|\mathbf{q}) + \tilde{E}_{\alpha\beta}(kk''|\mathbf{q})\}] \quad (1)$$

where M_k is the mass of the ion at the basis site $\mathbf{r}_k$, $C_{\alpha\beta}(kk'|\mathbf{q})$ is the usual Coulomb coupling coefficient between sublattices k,k', and $\tilde{E}_{\alpha\beta}(kk'|\mathbf{q})$ in the valence electron contribution, given by

$$\tilde{E}_{\alpha\beta}(kk'|\mathbf{q}) = \sum_{\mathbf{G}\mathbf{G}'}(\mathbf{q}+\mathbf{G})_\alpha(\mathbf{q}+\mathbf{G}')_\beta W_k(\mathbf{q}+\mathbf{G})W_{k'}(\mathbf{q}+\mathbf{G}')\chi(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')\exp\{i(\mathbf{G}\cdot\mathbf{r}_k - \mathbf{G}'\cdot\mathbf{r}_{k'})\} \quad (2)$$

where $\mathbf{G},\mathbf{G}'$ are reciprocal lattice vectors, $W_k(\mathbf{Q})$ is the pseudopotential form factor of the kth ion, and the valence electron density response matrix is given by

$$\chi(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}') = -\frac{1}{v(\mathbf{q}+\mathbf{G})}[\delta_{\mathbf{G}\mathbf{G}'} - \epsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')] \quad (3)$$

where $v(\mathbf{Q})$ is the Fourier transform of the effective electron–electron interaction (modified if necessary to include exchange and correlation corrections). $\chi(\mathbf{Q},\mathbf{Q}')$ measures the electron density response to an *external* (test-charge) perturbation.

Using the factorization approximation for $\epsilon(\mathbf{Q},\mathbf{Q}')$ discussed in references. (2–4), $\tilde{E}_{\alpha\beta}(kk'|\mathbf{q})$ can be reduced to the form

$$\tilde{E}_{\alpha\beta}(kk'|\mathbf{q}) = E_{\alpha\beta}(kk'|\mathbf{q}) - (\underset{\sim}{WSW^+})_{\alpha\beta}(kk'|\mathbf{q}) \quad (4)$$

where $E_{\alpha\beta}(kk'|\mathbf{q})$ is obtained by replacing $\epsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$ by $\{1/\epsilon_0(\mathbf{q}+\mathbf{G})\}\delta_{\mathbf{G}\mathbf{G}'}$ in equation (3) and then using equation (2). $\epsilon_0(\mathbf{Q})$ is the 'purely diagonal' part of $\epsilon(\mathbf{Q},\mathbf{Q}')$.[2–4] The matrices $W_{\alpha\beta}(ks'|\mathbf{q})$ and $S_{\alpha\beta}(ss'|\mathbf{q})$ have been defined in references (2–4). The sites s,s' are suitably chosen sites in the unit cell. As discussed in references (2–4), the physical assumptions of the model correspond to representing the electron density response in terms of distributions of dipoles at these sites, together with a screening medium possessing a diagonal screening function $\epsilon_0(\mathbf{Q})$. The polarizabilities associated with the dipole distributions are represented by the set of parameters $a_{\alpha\beta}(ss'|\mathbf{q})$. The above model also yields explicit expressions for the high frequency dielectric constant ϵ_∞, and the dynamical effective charge Z_k^* which have been given elsewhere.[3,4]

In order to simplify the model for the purpose of a practical calculation, certain simplifying assumptions were made, identical to those in the previously reported

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calculations.[2–4] Thus, the sites s were chosen to be the ionic sites; the $a_{\alpha\beta}(kk'|\mathbf{q})$ were taken to be of the form $a_1\delta_{\alpha\beta}\delta_{kk'}$; the pseudopotential form factor $W(\mathbf{Q})$ and the form factor $f(\mathbf{Q})$ characterizing the assumed dipole distributions were chosen as simple analytic functions[2–4] characterized by radii r_c, r_G respectively.

$\epsilon_0(\mathbf{Q})$ and a_1 were extracted iteratively from the function $\epsilon(\mathbf{Q},\mathbf{Q})$ by applying the acoustic sum rule, which reduces in the case of α-Sn to the condition $Z^* = 0$. As may be seen from Fig. 1, $\epsilon(\mathbf{Q},\mathbf{Q})$ is close to being an isotropic function of $\mathbf{Q}$, and accordingly was approximated as such after suitable averaging. Both the function $v(\mathbf{Q})$ and the RPA dielectric function calculated in Section 2 were modified to include exchange and correlation effects which were taken as those appropriate to a free electron gas of equivalent density, and of the form given by Singwi *et al.*[15] The parameter r_c was chosen so that the first node of $W(\mathbf{Q})$ coincided with that of the empirical pseudopotential for α-Sn given by Cohen and Heine,[13] although it was slightly modified to obtain the 'best fit' to the phonon spectrum. The radius r_G in $f(\mathbf{Q})$ was taken as an adjustable parameter.

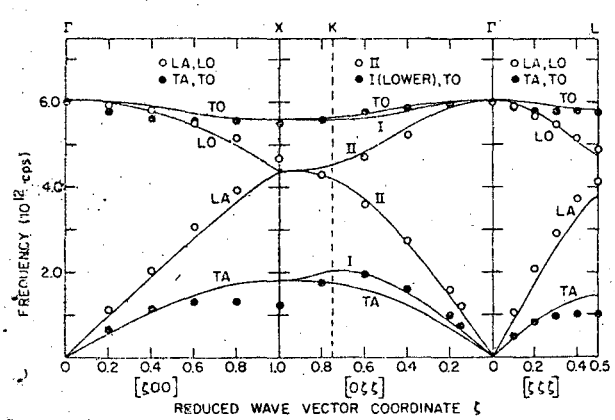

FIG. 2. The phonon dispersion curves for α-Sn calculated from the model, together with the experimental points of Price *et al.* (reference 16).

The resulting dispersion curves are shown in Fig. 2, along with the experimental points of Price *et al.*[16] The pseudopotential form factor $W(\mathbf{Q})$ used in the calculation is indicated in Fig. 3, together with the empirical points obtained by Cohen and Heine[13]

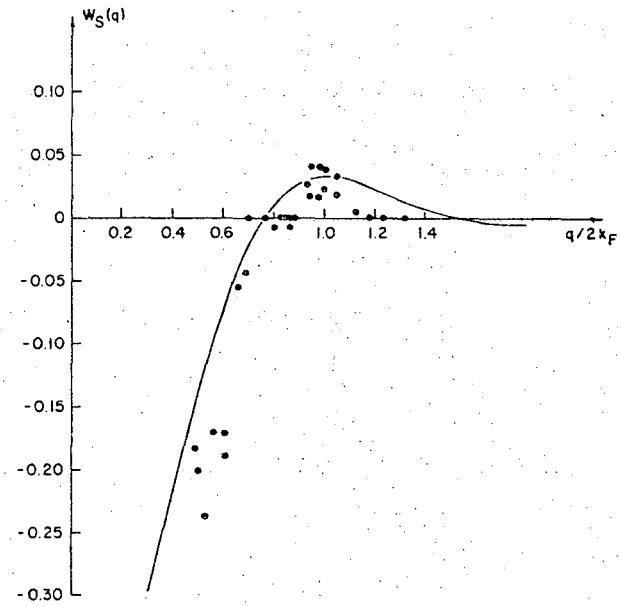

FIG. 3. Pseudopotential form factor for α-Sn used in the calculation. The curve shown corresponds to the bare ion pseudopotential screened by a free electron gas of equivalent density to that of the valence electrons in α-Sn. The points represent best fits to the band structure data as given by Cohen and Heine (reference 13).

from band-structure data. The value of ϵ_∞ calculated from the model is 16.6. The experimental value (extrapolated from measurements at 15μ incident wavelength) is 24.0. In this context, we may note that the best 11-parameter shell model fit to the data yielded a value for ϵ_∞ of 12.2.

The overall agreement with experiment is better in the case of α-Sn than for the corresponding calculations for Si and Ge.[2–4] We may note that a more accurate application of the formalism used here for covolent semiconductors would also necessarily include the bond-charge sites among the sites s, thus taking into account the tendency of the valence charge density to build up at these sites. In practice, a microscopic bond-charge model of this type would involve many more unknown functions and parameters and hence for simplicity we have chosen only spherically symmetric distributions (with form factors $f(\mathbf{Q})$ centered on the ionic sites. Such an approximation is probably better for α-Sn then the other group IV semiconductors in view of the more metallic nature of the bonding in α-Sn. A more detailed calculation would involve a knowledge of at least some of the off-diagonal elements of $\epsilon(\mathbf{Q},\mathbf{Q}')$.

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Die Dielektrischfunktion von α-Sn wurde mittels einer Pseudopotentialberechnung der Valenzelektroneneigenfunktionen und Energiebänder geschätzt. Zusammen mit einer Annäherungsmethode zur Berechnung der umgehrten Matrix der Dielektrischfunktion, wurde dies Ergebnis in einer Berechnung der Phononendispersionskurven angewendet. Die experimentellen und theoretischen Dispersionskurven stimmen im ganzen ziemlich gut überein.

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