Dielectric Matrix and Phonon Frequencies in Silicon

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(Received 14 April 1972)

The dielectric matrix $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ of a semiconductor is computed in the pseudopotential scheme. The result is applied to the calculation of the phonon frequencies in the [100] direction of Si. The presence of off-diagonal dielectric terms introduces long-range forces and leads to real TA frequencies, thus avoiding the necessity of introducing explicitly a bond-charge model.

The problem of calculating phonon frequencies in simple metals has been successfully solved in the pseudopotential approach. This method is essentially based on the linear screening of the electron-ion interaction, where only the diagonal part of the dielectric response matrix $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ is used to screen the pseudopotential. However, for semiconductors this technique fails, and in the case of diamond structure one obtains imaginary values of the transverse-acoustic (TA) frequencies,[1] even when a pseudopotential description holds. In fact, the dielectric properties of the valence electrons in a semiconductor are not well described, as in the case of simple metals, by a diagonal approximation of the dielectric matrix.[2,3] The Born–von Karman fitting performed by Herman[4] and the use of the Cochran shell model[5] have shown that distant-neighbor forces must be included in order to obtain the phonon frequencies of Si and Ge. More recently, the presence of long-range forces has been accounted for phenomenologically by the introduction of the Phillips bond charge[6] between ions. Martin[1] added the bond-charge contribution to the diagonal-screening-pseudopotential scheme, obtaining in this way a crystal stable against shear, i.e., real values of the TA frequencies. However, the bond-charge model should be related to microscopic dielectric screening in semiconductors, since it is clear that the piling up of charge along the bonds, due to constructive Bragg interference, is contained in the off-diagonal dielectric matrix elements.[6] Sinha, Gupta, and Price[7] made use of a model dielectric matrix containing the bond-charge model and a generalized shell model as particular cases, and showed that the latter picture provides a good fit to the phonon frequencies of Si.

An alternative way of accounting for the long-range forces in the lattice dynamics of semiconductors is to include terms beyond second order in the exact expansion of the dynamical matrix in powers of the electron-ion pseudopotential.[8] Soma and Morita (SM)[9] considered the third- and fourth-order contributions as given approximately in Si and Ge by an effective "enhancement" of the $\{220\}$ component of the pseudopotential, due chiefly to the large perturbation caused by the $\{111\}$ component.[10] By choosing an empty-core pseudopotential with free-electron screening, plus an electrostatic term representing point bond charges, they obtained force constants in real space, giving better agreement with the phonon spectra of Si and Ge than previous calculations.

In order to establish a direct connection between these descriptions of covalency effects and the dielectric approach, a closer investigation of the dielectric matrix of semiconductors based on the sole assumption of the validity of the pseudopotential scheme is desirable. The aim of this Letter is to calculate explicitly the off-diagonal elements of the dielectric matrix, and to show in the particular case of Si that their contributions to the dynamical matrix restores the stability of the crystal and accounts for the phonon frequencies.

The static dielectric matrix is given by

$$\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \delta_{\vec{G}\vec{G}'} - [4\pi e^2/(\vec{q}+\vec{G})^2\Omega]\pi(\vec{q}+\vec{G},\vec{q}+\vec{G}'), \quad (1)$$

where the polarizability (in the self-consistent–field approximation) is given in terms of the one-electron energies $E_{\vec{k}\vec{Q}}$ and of the periodic part of the Bloch functions $|\vec{k}\vec{Q}\rangle$ by[11,12]

$$\pi(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \sum_{\vec{k}\vec{Q}\vec{Q}'} \frac{f_0(E_{\vec{k}+\vec{q}\,\vec{Q}'}) - f_0(E_{\vec{k}\vec{Q}})}{E_{\vec{k}+\vec{q}\,\vec{Q}'} - E_{\vec{k}\vec{Q}}} \langle \vec{k}+\vec{q}\,\vec{Q}'|e^{-i\vec{G}\cdot\vec{r}}|\vec{k}\vec{Q}\rangle\langle\vec{k}\vec{Q}|e^{i\vec{G}'\cdot\vec{r}}|\vec{k}+\vec{q}\vec{Q}'\rangle . \tag{2}$$

Here $\vec{G},\vec{G}'$ and $\vec{Q},\vec{Q}'$ are reciprocal vectors; f_0 is the Fermi function; and Ω is the volume of the crystal. By assuming the validity of the nearly free-electron approximation for Si, we replace in Eq. (2) the true Bloch functions by the Brillouin-Wigner expansion for the pseudo wave functions

$$|\vec{k}\vec{Q}\rangle = e^{i\vec{Q}\cdot\vec{r}} + \sum_{\vec{Q}'\neq\vec{Q}} e^{i\vec{Q}'\cdot\vec{r}}(E_{\vec{k}\vec{Q}} - E_{\vec{k}\vec{Q}'}{}^0)^{-1}u(\vec{Q}'-\vec{Q}), \tag{3}$$

where $E_{\vec{k}\vec{Q}}{}^0$ are free-electron energies and $u(\vec{Q})$ is the local screened pseudopotential inclusive of the cell structure factor $S(Q)$. We approximate the off-diagonal π by a $\vec{k}\cdot\vec{p}$ expansion of $|\vec{k}+\vec{q},\vec{Q}\rangle$ around $\vec{q}=0$ and retain only the leading term in $\vec{q}$. This gives the essential contribution to the off-diagonal terms in lowest order as

$$\pi(\vec{q},\vec{q}+\vec{G}) = -\frac{\hbar^2}{m}\vec{q}\cdot\vec{G}u^*(\vec{G})\sum_{\vec{k}}\frac{f_0(E_{\vec{k}+\vec{G}}) - f_0(E_{\vec{k}})}{(E_{\vec{k}+\vec{G}} - E_{\vec{k}})(E_{\vec{k}+\vec{G}} - E_{\vec{k}}{}^0)^2} \equiv \epsilon(\vec{q}+\vec{G})\vec{q}\cdot\vec{P}(\vec{G}), \tag{4}$$

$$\pi(\vec{q}+\vec{G},\vec{q}+\vec{G}') = 2u(\vec{G}-\vec{G}')\left[\sum_{\vec{k}}\frac{f_0(E_{\vec{k}+\vec{G}}) - f_0(E_{\vec{k}})}{(E_{\vec{k}+\vec{G}} - E_{\vec{k}})(E_{\vec{k}+\vec{G}-\vec{G}'}{}^0)} + \text{the same with } \vec{G}\rightleftharpoons\vec{G}'\right] + O(q^2). \tag{5}$$

The expression for the diagonal π contains corrections which are proportional to u^2. In this case the main contribution arises from the highest valence band and the lowest conduction band. Since a restriction of expansion (3) to this pair of bands gives a result equivalent to that obtained by Penn,[12] we shall simply adopt for the diagonal dielectric function $\epsilon(\vec{q}+\vec{G}) \equiv \epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G})$ Penn's interpolation formula. The electronic part of the dynamical matrix[2,3]

$$D_{rr'}{}^{\alpha\beta} = \sum_{\vec{G}\vec{G}'}\left[f_{rr'}{}^{\alpha\beta}(\vec{q}+\vec{G},\vec{q}+\vec{G}') - \delta_{rr'}\sum_{r''}f_{rr''}{}^{\alpha\beta}(\vec{G},\vec{G}')\right],$$

$$f_{ss'}{}^{\alpha\beta}(\vec{q}+\vec{G},\vec{q}+\vec{G}') = [V_s(\vec{q}+\vec{G})V_{s'}(\vec{q}+\vec{G}')(\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta(\vec{q}+\vec{G})^2\Omega/4\pi e^2][\epsilon^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}') - \delta_{\vec{G},\vec{G}'}] \times \exp(i\vec{G}\cdot\vec{R}_s)\exp(-i\vec{G}'\cdot\vec{R}_{s'}), \tag{6}$$

is expressed in terms of the bare-ion pseudopotential V, the position of the ions $\vec{R}_s$ in the cell, and of the inverse dielectric matrix ϵ^{-1}. We invert our dielectric matrix analytically and retain only terms which give contributions up to the fourth order in V to the dynamical matrix. We regain in this way the $\vec{q}\to 0$ limit behavior given by Sham[2] with the explicit expression (4) for $\vec{P}$, as well as the acoustic sum rule. We compute expressions (4) and (5) by taking $E_{\vec{k}}$ to be the free-electron energy except for a gap $E_g = 0.11$ Ry outside a sphere of the Jones zone volume, and by approximating the screened pseudopotential $u(\vec{q})$ by its leading part $V(\vec{q})S(\vec{q})/\epsilon(\vec{q})$. Our choice for V is a Heine-Abarenkov pseudopotential with $A_2=3$, smoothed off at large wave vectors[1] to improve the convergence in the sum (6). We ensure the general consistency of our dielectric matrix by imposing the condition that the acoustical sum rule[2,3]

$$Z_s\delta_{\alpha\mu} = \lim_{\vec{q}\to 0}\alpha\sum_{\vec{G}}{}' V_s(\vec{q}+\vec{G})(\vec{q}+\vec{G})_\alpha P_\mu \exp(i\vec{G}\cdot\vec{R}_s) \tag{7}$$

should be satisfied. This is achieved by the introduction of the multiplicative constant α which turns out to be $\alpha_0 = 3.0$. The symmetry of the crystal requires that this factor α multiplies all the off-diagonal dielectric matrix elements. The arbitrariness in the choice of the potential especially for large wave vectors, the neglect of band effects on the electron energies, and our restriction to the first-order term[10] in the expansion (3) are clearly responsible for the deviation of α from 1. Fortunately, the fulfilment of the sum rule (7) allows us to overcome our approximations to a large extent, through the factor α_0, which enhances the off-diagonal terms of Eqs. (4) and (5). Had we adopted a free-electron, diagonal screening function, the acoustical sum rule would have been automatically fulfilled.[2] This choice is appropriate for SM's approach, but is not in a dielectric formulation for a semiconductor.

By extending the double sum in (6) up to 258 re-

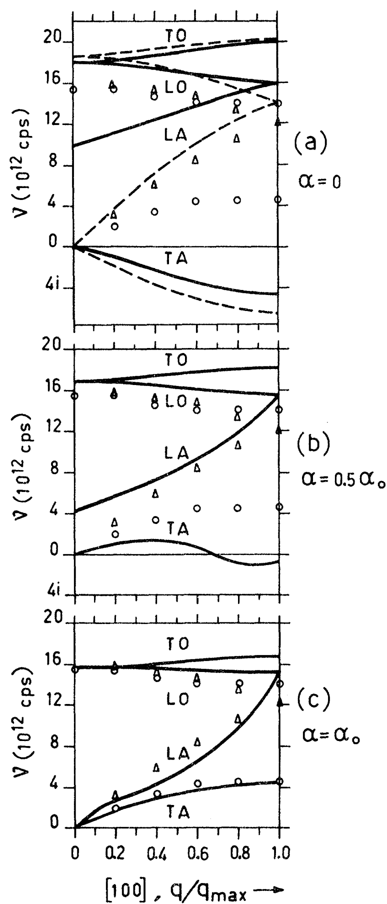

FIG. 1. Calculated phonon frequencies in the [110] direction of silicon. Experimental points are also given for comparison (from Ref. 13). (a) Dashed curves, Lindhard diagonal screening; solid curves, Penn diagonal screening. Both show imaginary TA phonon frequencies. (b) Half-strength off-diagonal screening, $\alpha = 0.5\alpha_0$. The change in the right direction can be noticed. (c) Final result, with full off-diagonal screening, $\alpha = \alpha_0$.

ciprocal vectors, we obtain our ultimate result of Fig. 1(c) for the phonon frequencies in the [100] direction of silicon. In analogy with SM, a substantial off-diagonal contribution originates from terms involving the pseudopotential components $\vec{G} - \vec{G}' = \{111\}$, but other components cannot be neglected because of their large number.

To show the effects of the off-diagonal screening on the phonon frequencies, we present in Figs. 1(a) and 1(b) the curves obtained by arbitrarily setting the "off-diagonal strength" α equal to zero and to one half of its full value. The phonons calculated with the Lindhard diagonal screening are also presented for comparison, in Fig. 1(a). They are basically the same as those of Martin,[1] displaying, as pointed out earlier, an imaginary TA branch. The case $\alpha = 0$ (solid lines) corresponds to replacing the Lindhard $\epsilon(\vec{q})$ with a Penn diagonal screening. We notice that even though this is the appropriate diagonal screening function for a semiconductor, the TA branch remains imaginary. In this case, obviously the $\vec{q} = 0$ LA frequency does not vanish but rather tends to a finite value because the ions are not completely screened. With the onset of the off-diagonal screening, the TA frequencies tend to become real and $\gamma_{LA}(0)$ decreases as shown in Figs. 1(b) and 1(c). The agreement of our phonon frequencies reported in Fig. 1(c) with the experimental results[13] is good for small q, and remains reasonable for the whole spectrum. The discrepancies arising especially in the LA branch for large wave vectors are clearly due to the $\vec{k}\cdot\vec{p}$ expansion involved in Eqs. (4) and (5), which holds exactly only for small $\vec{q}$. We notice that in spite of this crude approximation, the correct behavior of the off-diagonal corrections is not washed out even at the zone boundary. In particular, the TA branch, involving only the off-diagonal screening elements of type (5) whose q dependence is weaker, is brought from imaginary values to remarkably good agreement with experiment. In conclusion, we have shown how it is possible to obtain the correct behavior of the phonon frequencies of silicon from a microscopic pseudopotential approach which includes lattice effects on the screening. The existence of an effective charge pileup along the bonds due to the off-diagonal dielectric elements will be shown in detail elsewhere.[14] In our scheme we do not introduce bond charges phenomenologically, but rather justify microscopically the Phillips model, showing that the long-range forces arise directly from the contributions of these screening terms to the dynamical matrix.

Valuable discussions with Professor F. Bassani, Professor L. Falicov, and Professor F. Herman are gratefully acknowledged.

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Virtual-Bound-State–Induced Optical Absorptivity in CuNi Alloys*

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(Received 31 March 1972)

The optical absorptivity of dilute CuNi alloys at 4°K has been measured for photon energies between 0.1 and 3 eV and Ni concentrations between 0.5 and 4 at.%. The data are interpreted in terms of the Anderson model of magnetic impurities. A virtual bound state is found 0.75 ±0.02 eV below the Fermi energy with a half-width of 0.27 ±0.02 eV. The extra absorptivity of the alloy is found to arise predominantly from the scattering of the host conduction electrons in the presence of the virtual bound state.

In describing the electronic properties of metals containing transition element impurities, the concept of a virtual bound state[1] (VBS) has been useful. In the Friedel-Anderson[2] model, the VBS results from the mixing of the d levels of the impurity with the conduction electrons of the host producing a broadened peak in the electronic density of states of the alloy at energy E_d. The interpretation of certain physical properties[3] such as resistivity, specific heat, and thermopower in terms of the VBS theory allow estimates of the VBS energy E_d and half-width Δ. Yet these properties do not provide the best probe of the VBS because they are sensitive to the electronic structure only in the immediate vicinity of the Fermi energy. In principle, optical and photoemission studies can probe an energy range large enough to examine the detailed structure of the VBS, but there has been a notable scarcity of spectroscopic studies of metal alloys. Those experiments which have been performed were generally on high concentration samples (> 10 at.%) which do not really apply to the Friedel-Anderson model because of impurity-impurity interactions; moreover, because of difficulties in interpretation, only qualitative features of the VBS theory have been confirmed. Photoemission measurements,[4,5] however, have shown the appearance of an approximately Lorenzian density of states in the alloy, and recent calculations[6] of the alloy density of states using the coherent-potential approximation seem to be in remarkable agreement with the experimental results.

In this Letter we report an optical experiment on dilute CuNi alloys which can be quantitatively interpreted in terms of the VBS theory and provides an accurate measurement of the VBS parameters. We also show that the infrared absorptivity of CuNi alloys can be interpreted in terms of the Drude response of the free electrons of the host with a frequency-dependent relaxation rate due to the VBS.

The samples were prepared by simultaneous vacuum evaporation of the constituents onto a fused quartz substrate, 0.010 in. thick by 1 in. diam. Half the sample surface was pure Cu and the other half was the CuNi alloy. The deposition rates were typically 100 Å/sec (monitored with a quartz oscillator) and the total thickness was about 3000 Å. During the deposition the pressure was about 2×10^{-6} Torr and during the subsequent annealing (500°C for 15 min) about 5×10^{-7} Torr.

We use a low-temperature (4°K) calorimetric technique described by Hunderi[7] to measure the ratio of the alloy absorptivity to that of the pure metal (A_A/A_P). The quantity of interest in the experiment, however, is the differential absorptivity $\Delta A = A_A - A_P$. We therefore separately measured the absorptivity of our pure Cu films by comparison with gold black samples, finding good agreement with the results of Biondi and Rayne[8] on electropolished bulk samples.

The measured differential absorptivity for samples with nickel concentrations between 0.5 and