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Authors

Alvarez, Carmen Varea de
Cohen, Marvin L.

Publication Date

1973-10-01

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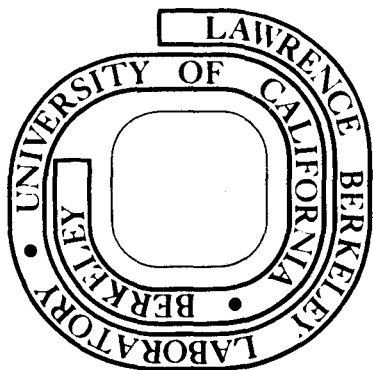
PRESSURE COEFFICIENTS FOR BAND GAPS IN SILICON

Carmen Varea de Alvarez and Marvin L. Cohen

October 1973

Prepared for the U. S. Atomic Energy Commission
under Contract 7405-ENG-48

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Pressure Coefficients for Band Gaps in Silicon*

Carmen Varea de Alvarez and Marvin L. Cohen

Department of Physics, University of California

and

Inorganic Materials Research Division, Lawrence Berkeley Laboratory

Berkeley, California 94720

Abstract

We have calculated the pressure coefficients of the main gaps in Si using the Empirical Pseudopotential Method (EPM). We find a trend toward metallization at high hydrostatic pressures. The deformation potential at the top of the valence band for uniaxial stress along the (0,0,1) direction is also obtained. All of the calculated pressure coefficients are in good agreement with experiment.

A large number of hydrostatic pressure experiments¹ have been carried out on the diamond type semiconductors. From them, the following rough "Empirical Rule" is found: the pressure coefficient of the energy difference between two states of a given symmetry is roughly independent of the material in which the pressure coefficient is measured. Here we present our theoretical results of the pressure coefficients of the main gaps in Si. The object of this calculation is three-fold: to attempt to understand why diamond type semiconductors transform as they do under

high hydrostatic stress; to investigate the "Empirical Rule"¹ and the correlation between a wave function $\psi_{\underline{k}}^n$ and the pressure coefficient of the energy level $E_{\underline{k}}^n$ for a given wave vector \underline{k} and given band n ; and to gain information about the "scaling" of the pseudopotentials through adjustments of our form factors using the experimental pressure coefficients.

Bassani and Brust² have calculated the pressure coefficients of the conduction band edges of Ge. Although their theoretical results are only in fair agreement with experiment, they do distinguish between sensitive and insensitive levels and show a definite correlation between pressure coefficients and the symmetry of the wave functions involved.

The method used in this work is the Empirical Pseudopotential Method EPM.^{3,4} The application of an external pressure modifies the pseudopotential form factors (and through them the electronic band structure $E_n(\underline{k})$) in the following ways:

(1) A change in the lattice constant changes the atomic volume so that the pseudopotential form factors $v(G)$ have to be scaled with inverse volume.

(2) A change in the lattice constant also changes the value of the reciprocal lattice vectors \vec{G} at which $v(G)$ has to be evaluated for the energy band calculation.

(3) A change in atomic volume is also expected to affect the screening of the valence electrons which in turn affects the functional dependence of $v(G)$. This effect is only big for small values of the wave vector q and of little importance for $\underline{G} \neq 0$.

From 1, 2, and 3 we see that in order to study the change in band structure with lattice parameter, it is necessary to know the complete pseudopotential function $v(q)$. In this paper we used an empirical approach to determine the slopes of $v(q)$ at the reciprocal lattice vectors \underline{G} at atmospheric pressure. The procedure is as follows: the pseudopotential curves were freehand extrapolated from their known values at atmospheric pressure. From the extrapolated curves the values of important gaps were obtained at 10 k bars (here we use the known compressibility of Si) and small adjustments to the extrapolation were made in order to have better agreement with experiment (at 10 k bars we are dealing with very small energy charges ≤ 0.1 eV, thus the results are very sensitive to the scaling). It is known that under very high pressures Si undergoes a phase transformation to a metallic phase similar to that of white tin; thus we are interested in exploring whether our simple method predicts a trend towards metallization for Si under high pressure. To do this, we adjusted a polynomial curve to the $v(q)$'s from the known values at the reciprocal lattice vectors at atmospheric pressure and at 10 k bars.

In EPM calculations, the importance of pressure experiments rests not only in the positive identification of important optical transitions in the electronic energy band structure of semiconductors; it also provides information on the scaling of the pseudopotential form factors. It is expected³ that the scaling that reproduces the pressure data for Si will give very good results when used to predict the band structure of Si in other crystalline phases (e.g. wurtzite). If in addition we know how to

scale P form factors from GaP pressure experiments and Zn form factors from ZnS pressure experiments, we are in a position to predict the electronic properties of the chalcopyrite compound ZnSiP_2 .⁵

We have applied the above scheme to silicon which is one of the solids for which the electronic band structure is best known; in addition, experimental data on Si under pressure¹ is readily available. The form factors⁴ for Si at 0 and 20 k bar pressure are (in Ry)

$$v(3) = -.21 \quad v(8) = .04 \quad v(11) = .0800$$

and

$$v(3) = -.2092 \quad v(8) = .044 \quad v(11) = .0816$$

respectively. In zincblende and diamond crystals, special attention has been paid to the study of the pressure coefficients of the first three valleys in the conduction band with respect to the top of the valence band at Γ . In Si, these three valleys have symmetry, L_1 , Δ_1 and Γ_{15} . Our calculated values for these pressure coefficients are (10^{-6} eV/bar)

$$\frac{dE_{\Gamma-L}}{dP} = 4.4 \quad \frac{dE_{\Gamma-\Gamma}}{dP} = -0.7 \quad \frac{dE_{\Gamma-X}}{dP} = -1.6 .$$

The experimental value for $\frac{dE_{\Gamma-X}}{dP} = -1.5 \times 10^{-6}$ eV/bar. The pressure dependence of the Γ -L transition is $\sim 5 \times 10^{-6}$ eV/bar for all zincblende (zb) and diamond crystals measured. The coefficient $\frac{dE_{\Gamma-\Gamma}}{dP}$ (i. e. $\Gamma_{25'} - \Gamma_{15}$) has not been measured. According to the

empirical rule, the pressure coefficient for the $\Gamma_{25}' - \Gamma_2'$ transition in zb and diamond crystals is $\frac{dE(\Gamma_{25}' - \Gamma_2')}{dP} \sim 10 \times 10^{-6}$ eV/bar (for Ge is 14×10^{-6} eV/bar) our calculated value is 13.4×10^{-6} eV/bar.

From the above theoretical and experimental results, it is clear that the pressure coefficients are quite sensitive to the symmetry of the wave functions. In Fig. 1 we show the absolute value of these wave functions as a function of position in the unit cell along the (1, 1, 1) direction. From this figure, we notice that the Γ_2' wave function is highly peaked near the atoms, the L_1 wave function is broader and also peaked at the atoms, the Γ_{15} wavefunction is concentrated at the antibonding site and the X_1 wavefunction is almost constant with a slight build up farther away from the antibonding site. It appears that the conduction band states with larger charge concentration at the atomic sites have larger pressure coefficients.

The calculated (at 100 k bar) pressure coefficients for the valence band states $\Gamma_{25}' - X_4$ and $\Gamma_{25}' - L_3'$ are -3.9 and -1.5 (10^{-6} eV/bar). For the important direct transitions (the ones that give the biggest contribution to the reflectivity spectra), $L_3' - L_1$ and $\Sigma_2 - \Sigma_1$ (0.4, 0.4, 0), our calculated value for the pressure coefficients are:

$$\frac{dE}{dP} (L_3' - L_1) = 5.7 \times 10^{-6} \text{ eV/bar}$$

$$\frac{dE}{dP} (\Sigma_2 - \Sigma_1) = 2.3 \times 10^{-6} \text{ eV/bar}$$

this last coefficient in fair agreement with the experimental value of $2.9 \pm 0.6 \times 10^{-6}$ eV/bar for the pressure coefficient of the main E_2 peak in reflectivity spectra.

The fact that negative pressure coefficients (with respect to the top of the valence band) are found for antibonding s-like states (Γ_{15}) and quasi-metallic states (X_1) in the conduction band, indicates that the total charge density $\rho(r)$ in the valence band should become more metallic as hydrostatic pressure is applied since this allows more mixing of these states with valence band states. To show this we calculated the charge density in our model for pressures of 0 k bar and 100 k bar. The charge density is calculated using the representative k-point used by Baldareschi.⁶

In Fig. 2, we show the charge density ρ (as function of position) for Si at 0 k bar of pressure. The agreement with Walter and Cohen's⁷ results is better than 3%. In Fig. 2, we also plot the quantity $\rho_{0 \text{ k bar}} - \rho_{100 \text{ k bar}}$, the results show a definite trend towards metallization. Since the main effect of pressure appears to be the transfer of charge from the atomic and bond sites to the antibonding region or other regions away from the atomic and bond sites, we can speculate that states which concentrate charge on these sites (e.g. Γ_2' , L_1) will have large pressure coefficients while states which concentrate charge away from the atomic and bond sites, (e.g. Γ_{15} , X_1) will have small pressure coefficients.

Using the scaling of the form factors obtained from hydrostatic pressure data, we also calculated the crystal field splitting at the top of the valence band for uniaxial stress along the (0,0,1) direction. This was done by diagonalizing the pseudopotential Hamiltonian of Si with a stress of $1-c/a = 0.025$. The value for the deformation potential $b(\Delta_{cr} = 3b(1-c/a))$ obtained is $b = -1.54 \times 10^{-6} \text{ eV/bar}$ in good agreement

with the experimental value of $b = -1.36 \times 10^{-6} \text{ eV/bar}$. This implies that the interpolation of the form factors is fairly good.

More experimental information on the hydrostatic deformation potentials of important gaps in zb materials would provide very useful information for the interpolation of the form factors. This information is essential when transferring the atomic pseudopotential form factors to a different environment.

Part of this work was done under the auspices of the U.S. Atomic Energy Commission.

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- * Supported in part by National Science Foundation Grant GP 35688
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Figure Captions

- Fig. 1. Magnitude of the wave functions at the top of the valence band and at several edges in the conduction band for Si along the (1, 1, 1) direction. The units are e per primitive cell.
- Fig. 2. Electronic charge density (along the (1, 1, 1) direction) in the valence band of Si at 0 k bars and the difference $\Delta\rho$ between this value and the charge density in the valence band of Si at 100 k bar. The units are e per primitive cell.

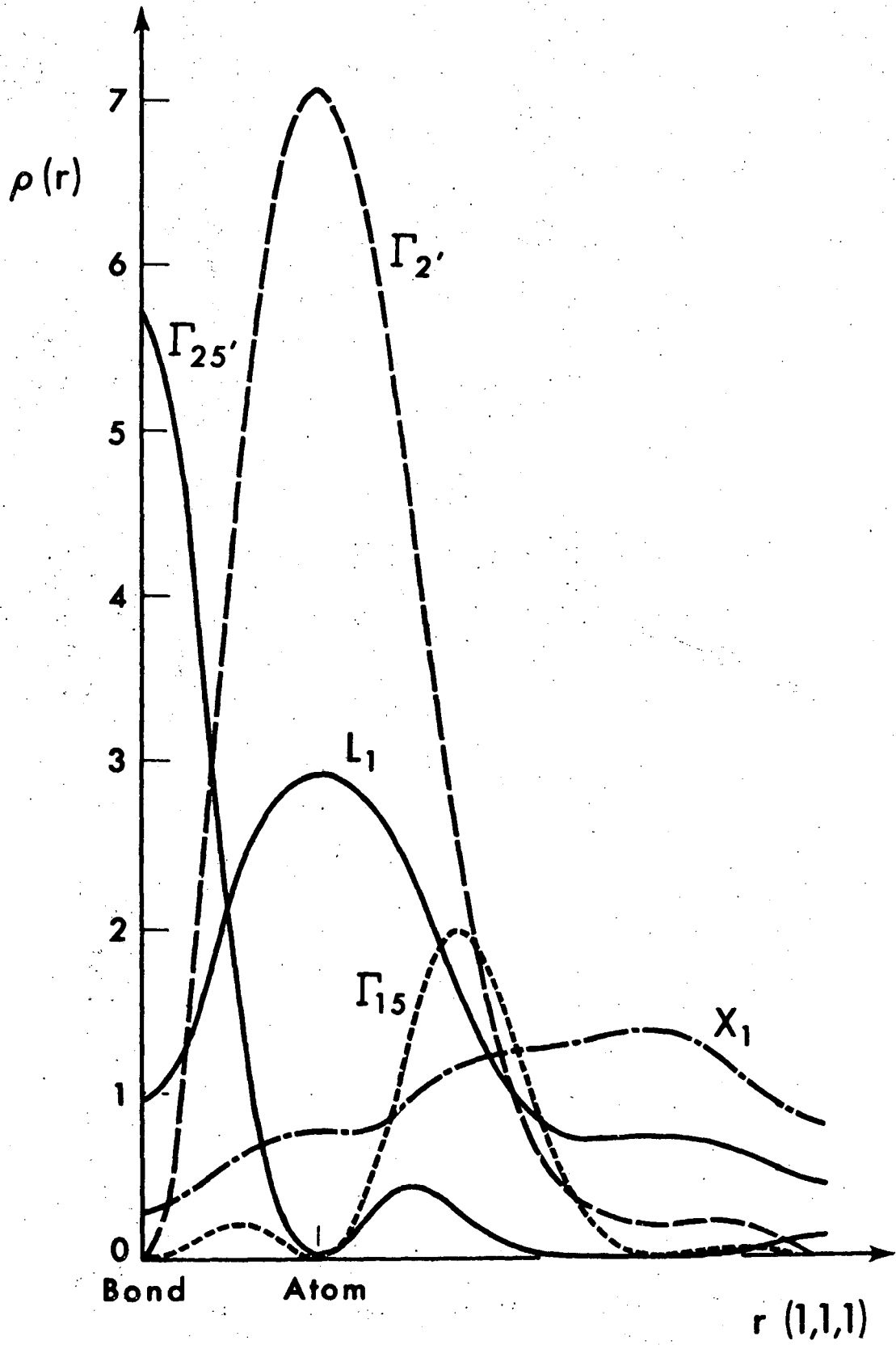


Figure 1

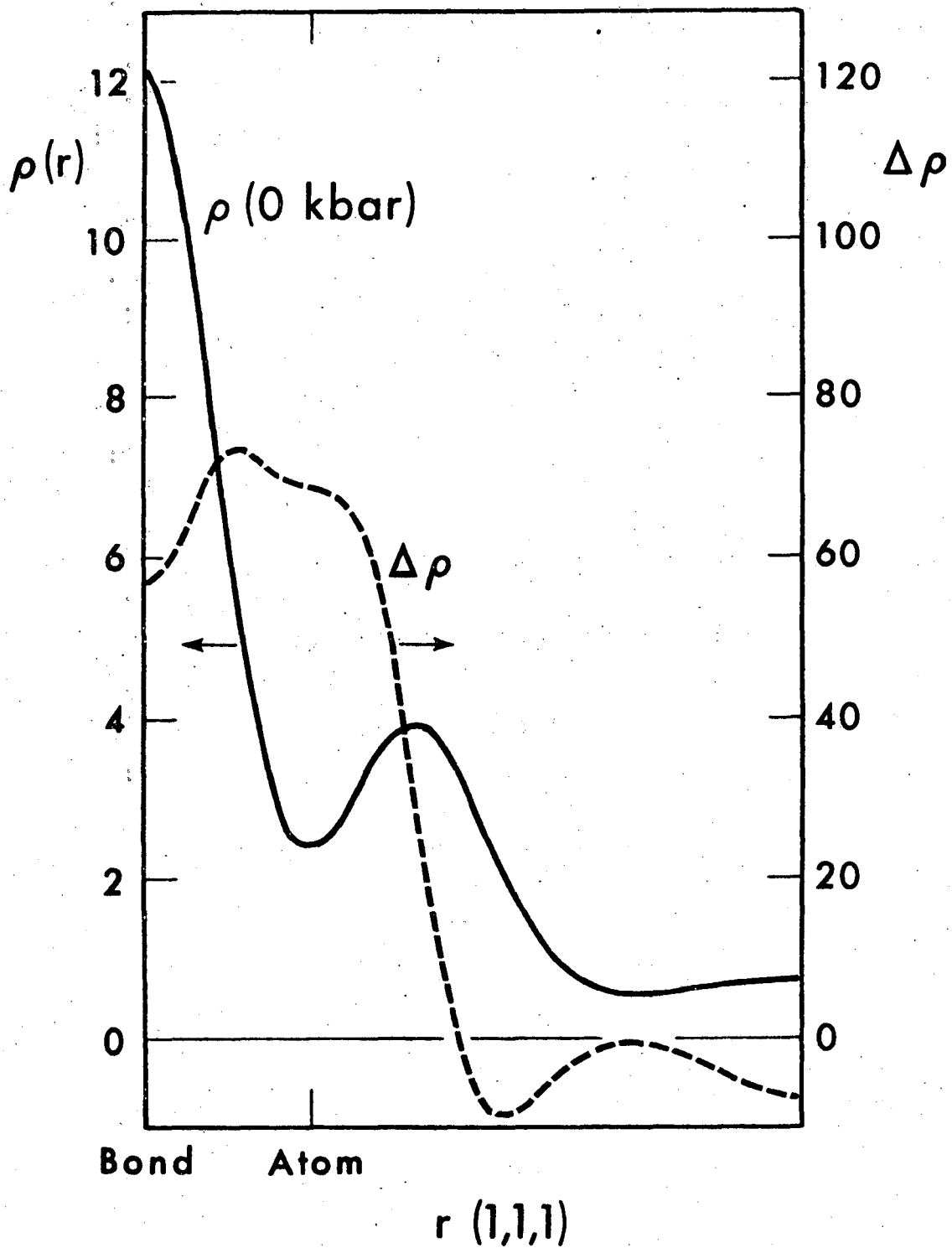


Figure 2

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