

fects) in the experiments of Sellers, Anderson, and Birnbaum<sup>2</sup> than in our experiments, in which internal stresses were more severe due to higher trap concentrations.

We would like to thank Professor G. Alefeld for many helpful discussions, and Dr. J. Völkl and his staff for their aid in sample preparation. We acknowledge the help of P. Zapp in the preparation of the manuscript, and financial support from the Bundesministerium für Forschung und Technologie.

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## Charge Density and Structural Properties of Covalent Semiconductors

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(Received 15 December 1977)

We propose a practical scheme to calculate structural energies in crystalline semiconductors. The method is applied to Si to calculate changes in charge densities and harmonic energies for TO( $\Gamma$ ), TA(X), and  $C_{11} - C_{12}$  distortions. Cubic anharmonic terms are also found for TO( $\Gamma$ ). For the shear modes a proper description of the electron-electron interaction is found to be vital. Electronic charge densities demonstrate the importance of dynamic redistribution of valence charge in covalent semiconductors.

In this Letter we introduce a practical scheme to calculate the charge density and total energy of crystals as a function of atomic displacements.

The method is not restricted to small displacements, and is here used to calculate directly from the electronic Hamiltonian both harmonic

and anharmonic energies. Employing calculation-appropriate procedures for the wide range of covalent semiconductors, we compute charge densities and from them total energies explicitly accounting for electron-electron interactions through direct Coulomb integrals and a local functional for exchange and correlation.<sup>1,2</sup> Energies for representative lattice displacements in Si are predicted and calculated results are given for the true charge redistributions, which previously have been approximated by phenomenological shells or bond charges.<sup>3,4</sup>

Structural properties of solids are derived from the total energy  $E_{\text{tot}}$  as a function of the positions of the nuclei.  $E_{\text{tot}}$  is a sum of a Coulomb interaction between the positive ions in a negative background,  $E_{\text{II}}$ , and an electronic part  $E_{\text{el}}$ . The latter is a unique functional of the charge density  $n(\mathbf{r})$ <sup>1</sup>

$$E_{\text{el}}[v, n] = \int v(\mathbf{r})n(\mathbf{r})d^3r + F[n], \quad (1)$$

where  $v(\mathbf{r})$  is the electron-ion interaction potential and  $F[n]$  is the energy functional comprised of kinetic and interaction energy of the electrons. The charge density  $n(\mathbf{r})$  is determined for a given  $v(\mathbf{r})$  by the variational condition that  $E_{\text{el}}$  is minimum for the correct  $n(\mathbf{r})$ . Structural energies are changes in the total energy calculated from the potentials  $v'$  and  $v$  and densities  $n'$  and  $n$ , respectively, of the distorted and the undistorted equilibrium systems

$$\Delta E_{\text{tot}} = \Delta E_{\text{II}} + (E_{\text{el}}[v', n'] - E_{\text{el}}[v, n]). \quad (2)$$

For small  $v' - v$ , Eq. (2) leads directly<sup>5</sup> to the general perturbation expressions<sup>4</sup> in terms of the linear dielectric response function  $\epsilon$ . In particular, this implies that all local-field effects<sup>4</sup> are included in Eq. (2).

In this paper we calculate structure energies from Eq. (2) using the local density approximation for exchange and correlation.<sup>2</sup> Then  $n(\mathbf{r})$  and  $E_{\text{el}}$  can be written in terms of the eigenfunctions  $\Psi_i$  and eigenvalues  $E_i$  of the now well-known band equations with a self-consistent effective one-particle potential  $\varphi(\mathbf{r})$ <sup>2</sup>:

$$n(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2, \quad (3)$$

$$E_{\text{el}}[v, n] = E_{\text{BS}} - E_{\text{EE}}[n],$$

where  $E_{\text{BS}} = \sum_i E_i$  and  $E_{\text{EE}}$  is the correction for over-counting electron-electron interactions in  $E_{\text{BS}}$ .<sup>2</sup> An essential aspect of Eqs. (1)–(3) is that  $n(\mathbf{r})$  must be computed self-consistently, given  $v(\mathbf{r})$ . The variational condition, however, shows

that any errors in  $n$  or  $n'$  make only second-order corrections to  $E_{\text{tot}}$ . In particular, if  $n$  for the undistorted crystal is self-consistent, then corrections to  $\Delta E_{\text{tot}}$  are second order in any error in  $n'$  and the approximate value for  $\Delta E_{\text{tot}}$  is always greater than the exact  $\Delta E_{\text{tot}}$ .

Evaluation of Eq. (3) is simplest for cases with crystalline periodicity. Then the sums for  $E_{\text{BS}}$  and  $n(\mathbf{r})$  are made over filled bands and wave vector  $\mathbf{k}$  and are readily evaluated by summing over lattices of "special points"<sup>6</sup> in the BZ (Brillouin zone). The lattices are determined by the symmetry of the distorted crystal, and the convergence in the lattice spacing indicates the range of interactions in real space.<sup>6</sup> In this manner, the calculations of  $n$  and  $E_{\text{tot}}$  reduce to carrying out ordinary band calculations at a few points in the BZ.

For our investigations we choose Si because it is a typical covalent semiconductor. Its electronic<sup>7</sup> and structural properties<sup>4</sup> are well known. Yet, to our knowledge no complete calculations of structural energies have been carried out. Previous calculations of phonon frequencies have approximated the screening function  $\epsilon^{-1}$  phenomenologically,<sup>4</sup> or expanded  $\epsilon^{-1}$  in powers of  $v$ ,<sup>4</sup> or have started from restricted tight-binding schemes.<sup>8</sup> Here we proceed directly from the electronic Hamiltonian. For our purposes it is sufficient to treat the core electrons as rigid, and for the potential  $v(\mathbf{r})$  we use the ionic model pseudopotential for  $\text{Si}^{4+}$  of Appelbaum and Hamann (AH).<sup>7</sup> We also take the AH local functional  $\epsilon_{\text{xc}} = 0.855(3n/\pi)^{1/3}$  for exchange and correlation. AH showed that for the undistorted crystal the self-consistent potential is very close to their starting guess  $\varphi(G) = v(G)/\epsilon_{\text{free}}(G)$  where  $\epsilon_{\text{free}}$  is the free-electron dielectric function derived with the same  $\epsilon_{\text{xc}}$ . Here the same starting form for  $\varphi$  is used and the energy is found to first order in self-consistency. That is, for both distorted and undistorted case we calculate  $n$  and  $n'$  from the approximate form for  $\varphi$  and use these densities in Eqs. (2) and (3). We have checked<sup>5</sup> to verify that the energies are insensitive to the precise forms of  $n$  and  $n'$ . Therefore, we expect the non-self-consistent results to be accurate with the one interesting exception discussed below.

With the above approximations we find the calculated equilibrium lattice constant to be 4.7 Å compared to the observed value of 5.431 Å. Similar results have been found in a fully self-consistent calculation.<sup>9</sup> We did not attempt to improve the result (see comment in Ref. 9) and for

the calculations described below, we corrected this defect by an *ad hoc* linear repulsive term between nearest neighbors to stabilize the lattice at  $a = 5.431 \text{ \AA}$ . Inclusion of this term corrects the restoring forces described below by canceling erroneous contributions caused by our system not being at the equilibrium position. The added term has no effect on the bulk modulus, which is  $7.0 \times 10^{11} \text{ dyn/cm}^2$  compared to the measured value  $9.79 \times 10^{11} \text{ dyn/cm}^2$ .

For representative distortions of the lattice we have chosen the modes  $\text{TO}(\Gamma)$  and  $\text{TA}(X)$  and the shear constant  $C_{11} - C_{12}$ . Calculations as a function of displacements have been carried out, and in Table I are given the contributions to the harmonic restoring forces in each case and the cubic anharmonic coefficient  $k_{xyz}$  for  $\text{TO}(\Gamma)$ . The contributions are divided as in Eqs. (2) and (3), and  $C$  denotes the correction from the linear term discussed above. This term contributes because of the change in first-neighbor distance to second order in the atom displacements. As we see, the calculated values agree with experiment well, except that the value for  $\text{TA}(X)$  is too large.

For the  $\text{TO}(\Gamma)$  mode, both the harmonic and the lowest-order anharmonic restoring forces for the TO phonon are dominated by ion-ion interactions whereas the band structure and electron-electron correction tend to cancel and play a secondary role.<sup>10</sup> Indeed, a second-order perturbation treatment of the valence charge<sup>5</sup> as well as a free-electron calculation<sup>4</sup> lead to very similar results. For the cubic force constant  $k_{xyz}$  our result is compared with that calculated from Keating's parameters,<sup>11</sup> which he derived by fitting experimental third-order elastic constants. The

sums over special points converged for the set corresponding to  $q = 2$  defined in Ref. 6 [requiring only (2) 3 inequivalent  $k$  points for the (un)-distorted lattice] showing that the range of important forces is  $\lesssim \sqrt{2}a$ . The redistribution of the valence electrons [Fig. 1(b)] in the TO mode reveals that the charge density in the stretched bond decreases compared to the equilibrium, and the charge density in the compressed bond increases. This also has been found in self-consistent calculations by Baldereschi and Maschke<sup>12</sup> and corresponds to the behavior that one expects from an overlap of bond orbitals.

Restoring forces for shear modes represented by  $\omega_{\text{TA}}$  at  $X$  and  $C_{11} - C_{12}$  are directly related to the directional covalent bonding. These modes are sensitive to the form of the electronic interactions since they are unstable in the free-electron approximation.<sup>4</sup> Also, it is interesting to compare  $2a(C_{11} - C_{12})$  and  $M\omega_{\text{TA}}^2$  because the large difference between these two quantities found experimentally implies forces beyond second neighbor.<sup>4</sup> It is these long-range forces which have led to the adiabatic shell and bond-charge models.<sup>3</sup> We see from Table I that II causes a large negative restoring force and that this is approximately canceled by the increase in BS for both modes. This is caused primarily by the increase in first-neighbor distance to second order in the shear atomic displacement, which is exactly the same for  $2a(C_{11} - C_{12})$  and  $M\omega_{\text{TA}}^2$ . It is only with inclusion of the EE term that these modes are even stable.<sup>10</sup> The result for  $2a(C_{11} - C_{12})$  is close to experiment and  $M\omega_{\text{TA}}^2$  is much smaller than  $2a(C_{11} - C_{12})$ , however the TA frequency is still about 40% too high compared to experiment.

TABLE I. Comparison of calculated and experimental harmonic force constants for  $\text{TO}(\Gamma)$ ,  $\text{TA}(X)$ , and  $C_{11} - C_{12}$  modes in Si (in  $\text{eV/\AA}^2$ ). Also given is the cubic anharmonic force  $k_{xyz}$  (in  $\text{eV/\AA}^3$ ) for  $\text{TO}(\Gamma)$ . It is compared with a value derived from Ref. 11. II, BS, and EE correspond to the separation of terms in Eqs. (2) and (3).  $C$  is the correction discussed in the text.

	$M\omega_{\text{TO}(\Gamma)}^2$	$2a(C_{11} - C_{12})$	$M\omega_{\text{TA}(X)}^2$	$k_{xyz}$
II	21.56	-29.25	-24.35	-69.92
BS	-5.76	27.62	20.70	18.62
EE	2.71	16.26	15.45	-1.16
$C$	-4.66	-6.98	-6.98	0
Total	13.85	7.65	4.82	-52.46
Expt.	14.00	7.32	2.33	(-40.51)

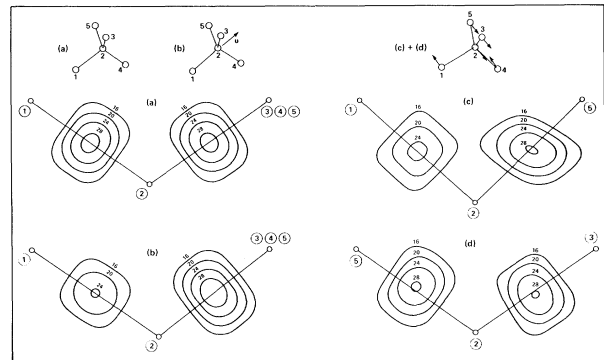


FIG. 1. Pseudo charge density in the bond region of crystalline Si: (a) undistorted lattice, (b)  $\text{TO}(\Gamma)$  phonon, and (c), (d)  $\text{TA}(X)$  phonon.

Two features indicate the nature of the forces: Convergence<sup>6</sup> for  $C_{11} - C_{12}$  required  $q = 4$  [(10) 20 points in the (un)distorted cases], whereas the TA required  $q = 3$  [(4) 6 points in the original fcc BZ]. Thus, long-range forces cause an increase in  $C_{11} - C_{12}$  with smaller effect upon  $\omega_{TA}$  in agreement with phenomenological models.<sup>5,13</sup> Secondly,  $C_{11} - C_{12}$  was relatively insensitive to  $n(r)$ , whereas  $\omega_{TA}$  depended greatly on the charge density  $n(r)$ ,<sup>5</sup> implying that the redistribution of charge is particularly important for the TA mode. The reason is indicated in the charge density plots in Figs. 1(c) and 1(d). For the TA distortion there are two inequivalent types of bonds: Type I maintains inversion symmetry and only the magnitude of the bonding charge decreases (for  $C_{11} - C_{12}$  all bonds are of this type). For bonds of Type II, the center of symmetry is lost, allowing an off-center charge relaxation shown in Fig. 1(d) reminiscent of a bond-charge displacement.<sup>3</sup> The changes in the magnitude and position of the maximum and the shape of the bond charge are sensitive to the effective potential  $\varphi(r)$ . This indicates self-consistency will be important, and, as we have shown above, this will lower the value for  $\omega_{TA}$ , bringing the theoretical result closer to experiment. Altogether, Figs. 1(c) and 1(d) show graphically the decrease in covalent bonding when the tetrahedral symmetry is destroyed, i.e., this is the basis of directional covalent "bond-bending"-type forces.

In conclusion, we have described a practical method for calculating structural energies in semiconductors within the local density functional formalism. Application of the scheme to TO( $\Gamma$ ), TA( $X$ ), and  $C_{11} - C_{12}$  atomic displacements in Si demonstrated the following: (1) Harmonic and anharmonic forces are predicted with no parameters. For TO( $\Gamma$ ) and  $C_{11} - C_{12}$  we find excellent agreement with experiment after the first step in the self-consistent procedure. The soft TA( $X$ ) mode is argued to require calculations carried further towards self-consistency. (2) From the convergence of the special-point summations we find the forces involved to be of short range in TO( $\Gamma$ ) and TA( $X$ ) and of longer range for the elastic  $C_{11} - C_{12}$  deformation. (3) Proper inclusion of electron-electron interactions is vital for stability against shear. (4) Dynamic charge redistribution has similarities with

phenomenological bond-charge models<sup>3</sup> but is much more complex in detail. Altogether the results presented here are encouraging and suggest a similar success of this scheme in other applications, e.g., in the study of surface reconstructions of semiconductors.

This work was supported by Deutsche Forschungsgemeinschaft.

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