spectra, but only smears them a bit. This interaction can, however, be responsible for the disagreement between photoemission experiments and band theory found in ferromagnetic materials.[18,19]

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Electronic Charge Densities and the Temperature Dependence of the Forbidden (222) Reflection in Silicon and Germanium*

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Using nonlocal pseudopotentials for silicon and germanium we are able to calculate the temperature dependence of the forbidden (222) reflection and we find it to be in excellent agreement with experiment. The accuracy of the pseudocharge density for the case of silicon is also examined and found to be in good agreement with recent x-ray experimental results.

Remarkable progress has recently been made in the measurement of charge distributions in crystalline silicon and germanium.[1-6] These exceedingly precise measurements, in the case of silicon, have allowed the valence charge density to be accurately determined for the first time.[5] Such measurements are, of course, of considerable value not only as a means of ascertaining the accuracy of band-structure calculations and the resulting wave functions, but as a means of better understanding the bonding process itself. In this context there has been much interest in determining the behavior of the valence charge density, and in particular the bonding electrons, as a function of temperature. By combining neutron and x-ray diffraction studies, Roberto, Batterman, and Keating[6] have been able to establish the temperature dependence of the "forbidden" (222) reflection in both silicon and germanium, and specifically, they have been able to determine the relative contributions to the forbidden reflection arising from the bonding electrons and from the anharmonic motion of the ion cores.

From a theoretical point of view, while the use of pseudopotentials has been well established in the calculation of charge densities, only recently has it been possible to compare the results directly with experiment. Such a comparison, in

the case of silicon, has indicated that the pseudocharge density while adequately reproducing the bond maximum and magnitude fails to yield the correct bond shape.[5] However, we shall demonstrate that this discrepancy is not a serious one, and that it is a direct consequence of the local-pseudopotential approximation. The discrepancy is eliminated through the use of an energy-dependent nonlocal pseudopotential. In addition, for the first time, a calculated temperature dependence for the forbidden (222) reflection is found to be in excellent agreement with experimental results. Early attempts[2] to account for the temperature dependence were based on inaccurate experimental results,[6] and are not in accord with the more recent data. More recent simplified models have also failed at the higher temperatures.[6] As suggested by Phillips[7] and Roberto, Batterman, and Keating,[6] we find that the change in bonding charge with temperature is significant. Further, we find, under the assumption of an Einstein solid, that the Debye-Waller factor characteristic of the bond motion is one-half that of the ion cores.

In establishing the temperature dependence of the bonding charge the anharmonic contribution from the ion motion must be subtracted out from the "forbidden" (222) reflection.[6] This may be accomplished through the use of neutron diffraction techniques as neutrons interact primarily with the nuclei. In such a fashion, using the simple model of Dawson and Willis[8] to account for the temperature dependence of the ion-core contributions, Roberto, Batterman, and Keating have separated out the anharmonic motion of the cores. Once this has been accomplished the resulting contributions to the forbidden reflection can arise only from noncentrosymmetric parts of the charge density, i.e., bonding charge.

Since the "forbidden" (222) reflection, corrected for the anharmonic motion of the ions, depends upon the structure factor $F_{222}{}^{b}$ for the bond, the temperature dependence of this reflection can be analyzed in terms of this "bond" structure factor. The procedure which we shall follow in obtaining the temperature dependence of the structure factor for the bond will be analogous to a rigid-atom model.

In this model the structure factor is the product of two factors: the Fourier transform of the charge distribution, or scattering factor, and a Debye-Waller factor. The first factor accounts for the charge distribution, the second for thermal motion. To calculate the structure factor for the bond we first calculate the charge distribution with the ion cores in their equilibrium positions and determine the scattering factor for the bond. Next we take the bond motion into account by an appropriate Debye-Waller factor, and obtain the structure factor for the bond by the product of the scattering and Debye-Waller factors. However, unlike the atomic case we take into consideration the effect that the bonding charge may be significantly altered by temperature as suggested by Phillips.[7] In order to account for this change in bonding charge, and the resulting change in the scattering factor, we calculate the effect of temperature on the crystalline potential. This may be done in a straightforward manner involving the use of the Debye-Waller ion-core factors as indicated by Walter *et al.*[9]

In obtaining the effect of temperature on the charge density it is necessary to have a knowledge of the crystalline potential, the thermal expansion function of the solid, and the phonon spectra of Debye-Waller factors for the ion cores.[9] These data, however, are well established for both silicon and germanium. Recent calculations on both silicon[10] and germanium[11] using nonlocal pseudopotentials have been able to obtain accurately the optical gaps, photoemission results, and cyclotron masses, and these are the potentials which we shall use in the present calculation. Further, the thermal expansion function has been tabulated over an extensive temperature range[12] and Batterman and Chipman[13] have incorporated x-ray data on the ion-core motion into Debye-Waller factors for both crystals.

After the scattering factor has been calculated in the manner outlined above, it is necessary to obtain a Debye-Waller factor for the bonding charge. Welsh has suggested that the Debye-Waller factor appropriate for the bonding charge should be smaller than the corresponding Debye-Waller factor for the ion cores.[6] However, under the physically reasonable assumption that the motion of the bond should be characterized by the motion of the midpoint of near-neighbor atoms, and the additional assumption of an Einstein solid (appropriate for the temperatures involved[13]), it is easy to demonstrate that the Debye-Waller factor for the bond is exactly one-half that for the ion cores.

The results of our calculations are given in Fig. 1 for silicon and Fig. 2 for germanium. Also indicated are the results from the simple model of Roberto, Batterman, and Keating,[6] which assumed that the valence charge density was not

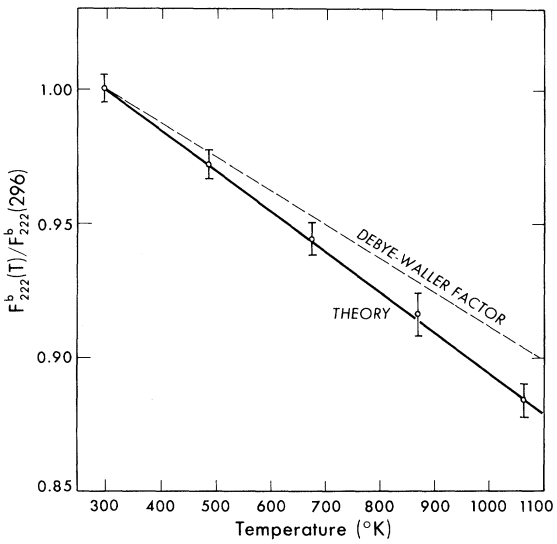

FIG. 1. The temperature dependence of the structure factor $F_{222}{}^b$ for silicon. The experimental data points are from Roberto, Batterman, and Keating (Ref. 6). The solid line shows the temperature dependence as calculated by a nonlocal pseudopotential, and the dotted line indicates the temperature dependence of the Debye-Waller factor for the ion core as used by Roberto, Batterman, and Keating.

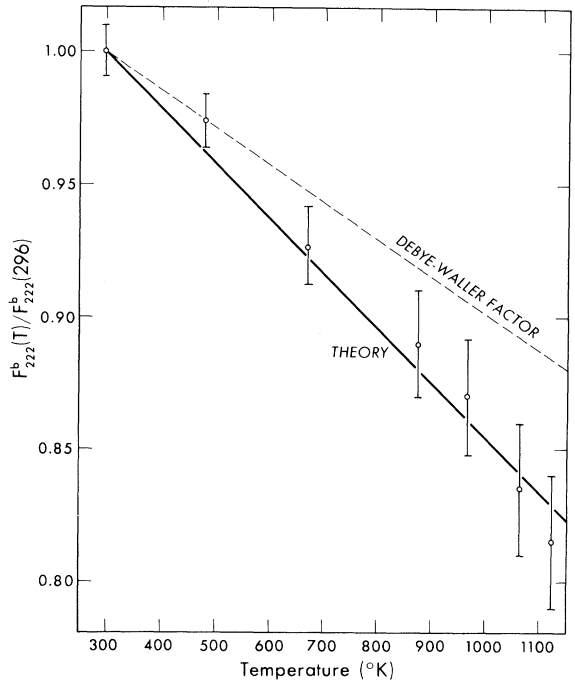

FIG. 2. The temperature dependence of the structure factor $F_{222}{}^b$ for germanium. The experimental data points are from Roberto, Batterman, and Keating (Ref. 6). The solid line shows the temperature dependence as calculated by a nonlocal pseudopotential, and the dotted line indicates the temperature dependence of the Debye-Waller factor for the ion core as used by Roberto, Batterman, and Keating.

altered by temperature. They also assumed that the bond motion would be that of the ion cores and, hence, that the same Debye-Waller factor could be used. Unlike their results, our calculations are in excellent agreement over the entire temperature range for both silicon and germanium. However, it should be pointed out that Roberto, Batterman, and Keating recognized quite clearly the drawbacks of their model and, in fact, suggested that the temperature dependence of the scattering factor, or charge density, combined with a reduced Debye-Waller factor for the bond motion might yield the correct temperature dependence for the "bond" structure factor.

We also mention in this context that Phillips[7] has suggested that a decrease in the bonding charge, Z_b, alone could account for the observed temperature dependence of the structure factor. He has developed a theory for the magnitude of the bonding charge which states that it should vary as the inverse square of the optical constant, i.e., $Z_b \propto n^{-2}$. If we evaluate $\Delta Z_b/Z_b$ in terms of finite differences over the temperature range of interest we find $\Delta Z_b/Z_b = 0.066 \pm 0.006$ for silicon and $\Delta Z_b/Z_b = 0.13 \pm 0.05$ for germanium, using the experimental values of $n(T)$.[14] If we associate the (222) component of the charge density, ρ_{222}, as a measure of the bonding charge, and evaluate $\Delta\rho_{222}/\rho_{222}$, we find $\Delta\rho_{222}/\rho_{222} = 0.062$ for silicon and $\Delta\rho_{222}/\rho_{222} = 0.099$ for germanium in good accord with the values predicted by Phillips. The values, however, for $\Delta F_{222}{}^b/F_{222}{}^b$ are 0.10 ± 0.01 for silicon and 0.18 ± 0.02 for germanium. Therefore, we note, at least in the case of silicon where the experimental values are determined with more precision than in germanium, that the decrease in Z_b alone cannot adequately explain the observed temperature dependence of the forbidden (222) reflection. However, if a Debye-Waller factor appropriate for the bond is included, then Phillips's predicted values for $\Delta Z_b/Z_b$ can adequately account for the observed behavior.

In Fig. 3 we compare the experimentally determined valence charge density for silicon with the results of an energy-dependent nonlocal pseudopotential. The results are similar to a previous charge-density calculation using a local pseudopotential by Walter and Cohen[15] in that the bond maximum lies at the midpoint between neighbor-

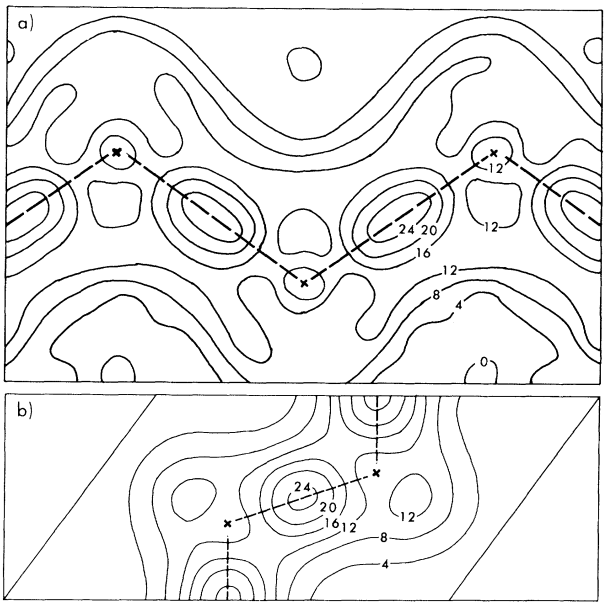

FIG. 3. (a) The valence charge density for silicon as determined from experimental data by Yang and Coppens (Ref. 5) (in the plane of the bonds). (b) The valence charge density as calculated by a nonlocal pseudopotential in a section of the same plane. The crosses label the atomic sites.

ing atoms, and the value of the bond maximum is the same. Both of these results are in good accord with experiment (the bond maxima are $26e/\Omega_c$ for both theoretical calculations and $28e/\Omega_c$ for experiment). However, as Yang and Coppens[5] have noted, the local-pseudopotential result has an incorrect bond shape in that the bond axis runs perpendicular to the bonding direction.[15] Further, they point out that such a discrepancy is far beyond the limits of experimental error. The energy-dependent nonlocal pseudopotential, on the other hand, has the correct bond shape; in this case the bond axis is elongated parallel to the bonding direction. This rotation of the bond can be traced to the effect of the energy-dependent part of the nonlocal pseudopotential on the bottom valence band. The need for an energy-dependent nonlocal pseudopotential is also indicated by spectroscopic[16] and photoemission data.[10]

Finally we mention that the accuracy of our pseudocharge-density calculation in yielding an accurate temperature dependence for the forbidden (222) reflection and in producing an accurate valence charge density is quite encouraging. We expect the pseudocharge density to fail to reproduce the actual charge density in the core region; however, that it is so accurate away from the core region, i.e., the bonding region, suggests that other band calculations can be refined to give similar results; e.g., self-consistent orthogonalized-plane-wave results[17] have, thus far, not yielded accurate structure factors.

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