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Nonlocal pseudopotentials for Ge and GaAs

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Nonlocal pseudopotentials are constructed for Ge and GaAs. Agreement with interband optical edges in the region 0–7 eV is achieved to within 0.05 eV. The by-products of the calculation are: an improved fit to valence-band edges as measured by photoemission; an improved critical-point topology for the energy difference between the lowest conduction and highest valence bands; and more significant local-pseudopotential parameters.

I. INTRODUCTION

Experimental information on the electronic structure of semiconductors has become much more precise and more abundant in the last five years. Although the general outlines of the subject were established by spectroscopic studies[1] of direct interband spectra in the early 1960's, more recent interband data obtained by refined modulation techniques[2] have confirmed earlier assignments, established more precise values for interband energies, and removed ambiguities of interpretation that could easily arise at higher energies where several different interband transitions were nearly degenerate in energy. At the same time photoemission data in the far uv have been collected which have been interpreted as yielding images of the bulk density of states in the valence band.[3] At photon energies in the 10–30-eV range, lifetime broadening becomes a more serious problem than it was at energies near 5 eV or less, so that the photoemission data are inherently less accurate than data obtained by modulation spectroscopy. Moreover, corrections to the bulk density of states resulting from final-state interactions (Coulomb attraction of excited electron-hole pairs) and from surface resonances[4] add further complications to the interpretation of photoemission data.

Systematic surveys of the electronic structure of a number of tetrahedrally coordinated semiconductors were last reported using local pseudopotentials[5] and empirically adjusted orthogonalized-plane-wave calculations.[6] Unfortunately, many "first-principles" band calculators have chosen to ignore experimental data or brush it aside in reporting isolated studies of the electronic structure of even such simple cases as Si, so that since 1968 little theoretical progress has accompanied the refinement of experimental data.

Perhaps the simplest refinement of the local-pseudopotential method is to add an energy-dependent term which modifies the kinetic energy by replacing $p^2/2m$ (where m is the free-electron mass) by $p^2/2m^*$. This correction has been suggested by several authors,[7] and it has the merit of involving only one additional adjustable parameter. It also makes it possible to increase the width of the valence band in a simple manner, bringing all the valence-band energies into better agreement with photoemission data.[3] This refinement was also considered by us, but it was rejected for several reasons. First, there is no physical justification for replacing m by m^*. Second, from the empirical point of view this refinement is unsatisfactory, because the sign of $m - m^*$ required to fit the valence-band widths is opposite to the one needed to improve agreement on interband energies, especially the higher ones (E_0', E_2, and E_1' in Cardona's notation). See Appendix A for a detailed discussion of this point.

A simple one-parameter refinement which improves valence band widths and higher interband energies in Ge *simultaneously* is based[8] on the use of a nonlocal term V_d to represent repulsive effects from the $3d$ core states that exist over and above those already contained in the local pseudopotential. Such effects were previously known[9] to be large in Cu. If we consider the isoelectronic sequence Ge, GaAs, ZnSe, CuBr, one would expect the magnitude of the nonlocal d repulsive potential $V_d^{A,B}$ to increase on the cation A and decrease on the anion B throughout this sequence, and one can hope that careful fitting of the experimental data in GaAs will reveal this trend.

The most significant limitation in a semiempirical study of this kind is the number of parameters required. If this number is too large, then the parameters will be underdetermined. Some ambiguities can be resolved by analyzing trends in a number of related compounds, and demanding that these be consistent with the chemical valence concepts.

One of the earliest discoveries of the pseudopotential method was that only three orbital parameters, denoted by $V^s_{G^2}$, with $G^2=3$, 8, 11 [in units of $(2\pi/a)^2$] were required[10] to determine satisfactory band structures for Si and Ge. Although V^s_{11} is not small, the fitted band structures obtained using three additional parameters (corresponding to $G^2=12$, 16, and 19) were found[11] to be little different from the original ones. The three higher coefficients, although not weak, are nearly linearly dependent on the three lower ones in their effect on the band structure. The same is true of increasing the number of plane waves, i.e., so far as V^s is concerned, convergence is not a serious problem, as long as the maximum size of the basis set involves of order 70–100 plane waves.

As soon as we add a second element, the number of adjustable parameters[5] is doubled: to the elemental parameters V^s_3, V^s_8, and V^s_{11} we must add V^a_3, V^a_4, and V^a_{11}, the superscripts referring to components of the crystal potential that are either symmetric or antisymmetric with respect to interchange of the two atoms in the unit cell. We assume, as before, that no qualitatively new results would be obtained from $V^a_{G^2}$ with $G^2 \geq 12$. This assumption should be valid so long as $|V^a_3| \lesssim |V^s_3|$.

Even with this simplifying assumption, there are now six adjustable parameters rather than three. Whereas the three parameters $\{V^s_{G^2}\}$ are overdetermined in Si and Ge, the six parameters $\{V^s_{G^2}, V^a_{G^2}\}$ may be underdetermined in sphalerite compounds $A^N B^{8-N}$. This problem was recognized and circumvented to some extent by Cohen and Bergstresser,[5] who chose parameters in fourteen $A^N B^{8-N}$ compounds in a systematic manner consistent with chemical trends. Nevertheless, the adequacy of their determination of $\{V^s_{G^2}, V^a_{G^2}\}$ was limited, especially by the extent of the data available to them in 1966.

How is this situation changed by new data[2,3] and by the improved fit[8] to the energy bands of Ge using the nonlocal potential $\{V^s_{G^2}, V_d\}$? Values of V_{G^2} can also be obtained from the model free-atom nonlocal form factors $V^{\text{nonl}}_{\text{mod}}$ adjusted to fit free-atom term values by Heine and Animalu.[12] The nonlocal operators are transformed to local ones on the Fermi surface. When this transformation is also applied to the semiempirical parameters $\{V^s_{G^2}, V_d\}$ to obtain $V^{\text{equiv}}_{\text{loc}}$, better agreement is found with $V^{\text{loc}}_{\text{mod}}$, especially for $G^2=8$ and 11, than was obtained by Cohen and Bergstresser with the entirely local empirical parameters $\{V^s_{G^2}\}$. If we regard $V^{\text{loc}}_{\text{mod}}$ as given (because it is based not on the crystalline electronic structure, but on free-atom term values), this leads to a number of arbitrarily adjustable parameters in $\{V^s, V_d\}$ which is less than in $\{V^s\}$ alone. Moreover, the fit to the electronic structure of Ge is much improved.

Turning now to GaAs, we see that there is a reasonable expectation, in spite of the increased number of parameters contained in $\{V^s_{G^2}, V^a_{G^2}, V^A_d, V^B_d\}$, that these parameters can be determined in a physically meaningful way. The difference between the parameters for GaAs and for Ge, as measured by $V^a_{G^2}$ and $V^A_d - V^B_d$, is then a direct measure of ionic effects in the crystal.

II. LOCAL AND NONLOCAL POTENTIALS

In a diatomic crystal one can choose the origin of coordinates halfway between the two atoms in the unit cell. Then the local pseudopotential can be written in terms of reciprocal lattice vectors $\vec{G}$ as[5]

$$V(\vec{r}) = \sum_{|\vec{G}|^2 \leq 11} (\cos\vec{G}\cdot\vec{\tau}\, V^s_G + i\sin\vec{G}\cdot\vec{\tau}\, V^a_G)\, e^{-i\vec{G}\cdot\vec{r}}, \quad (1)$$

with the symmetric and antisymmetric form factors V^s_G and V^a_G given in terms of the atomic form factors $V_A(G)$ and $V_B(G)$ by

$$2V^{s,a}_G = V_A(G) \pm V_B(G)\ , \quad (2)$$

with the atomic form factors given in terms of atomic pseudopotentials by

$$V_A(G) = \frac{2}{\Omega}\int V_A(r)\, e^{i\vec{G}\cdot\vec{r}}\, d^3r\ , \quad (3)$$

where Ω is the volume of the unit cell. In Eq. (2) it is assumed that the total crystal potential can be represented as a superposition of spherically symmetric, overlapping potentials $V_{A,B}(r)$ centered on the A, B sublattices. This is true of the ion-core potentials, and it turns out that it is also true of the valence electron contributions to $V^{s,a}_G$ for $G^2 \leq 11$, provided small empirical corrections are made to these quantities.

The nonlocal part of the atomic pseudopotential is written as

$$V_A(\vec{r}) = \sum_l V_l(r) P_l\ , \quad (4)$$

where P_l is the projection operator[13] on the subspace Y_{lm} ($m=-l$ to $+l$) of spherical harmonics with the same l and

$$\begin{aligned} V_l(r) &= A_l \quad r \leq R_l \\ &= 0 \quad r > R_l\ . \end{aligned} \quad (5)$$

The matrix element of V_A between plane waves normalized to the volume Ω is

$$\begin{aligned} \langle \vec{k}' | V_A | \vec{k} \rangle = \frac{4\pi}{3\Omega} \sum_l (2l+1) P_l \\ \times (\cos\theta_{k'k}) A_l R_l^3 F_l(x, x')\ , \end{aligned} \quad (6)$$

where the function $F_l(x,x')$ is given in terms of $x = kR_l$ and $x' = k'R_l$ by $(x \neq x')$

$$\begin{aligned} F_l(x,x') = [3/(x^2 - x'^2)] \\ \times [x j_{l+1}(x) j_l(x') - x' j_{l+1}(x') j_l(x)]\ , \end{aligned}$$

$$F_l(x,x) = \tfrac{3}{2}[j_l^2(x) - j_{l-1}(x) j_{l+1}(x)] \ . \qquad (7)$$

The explicit form of (7) in terms of the spherical Bessel functions $j_l(x)$ depends on the square-well form used in (5). With k and k' near k_F (the Fermi wave number of a free-electron gas with density equal to that of the valence electrons) and R_l close to the atomic radius, x and x' are near 3.5, which is close to the first maximum of $j_2(x)$. Thus for initial and final states with energy close to E_F, $F_2(x, x')$ is positive and is not strongly sensitive to the square-well function used in (5).

III. ENERGY BANDS OF Ge

In a preliminary report[8] we showed that the three-parameter local pseudopotential[5] energy bands for Ge could be brought into much better agreement with experiment by the addition of a nonlocal $l = 2$ repulsive pseudopotential. In obtaining the parameters for that pseudopotential, we assumed that the critical-point topology[14] of the nonlocal energy bands would be essentially the same as that of the bands derived from the local pseudopotential. This assumption has proved to be incorrect, with the result that the parameters for Ge reported here are slightly different from those reported earlier.

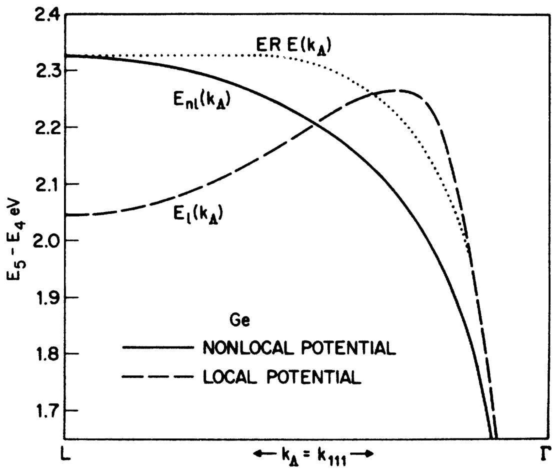

FIG. 1. Comparison of $E(\vec{k}) = E_5(\vec{k}) - E_4(\vec{k})$ as given by the nonlocal pseudopotential for Ge described here with the local pseudopotential for Ge of Ref. 5. The wave vector $\vec{k} = k_\Lambda = k_{111}$ varies along the line Γ and L. Also shown is the "nearly flat" curve for $E(\vec{k})$ along this axis as suggested by analysis of electroreflectance (ER) data. Not that $E_{nl}(k_\Lambda)$ is much more nearly flat than $E_l(k_\Lambda)$, and is thus in much better accord with the experimental line shape for the interband absorption edge near 2 eV. [In this figure, as throughout the paper, the effects of spin-orbit splitting are omitted. All the curves shown therefore represent, to a good approximation, the center of gravity of $E_5(\vec{k}) - E_4(\vec{k})$ and $E_5(\vec{k}) - E_3(\vec{k})$.]

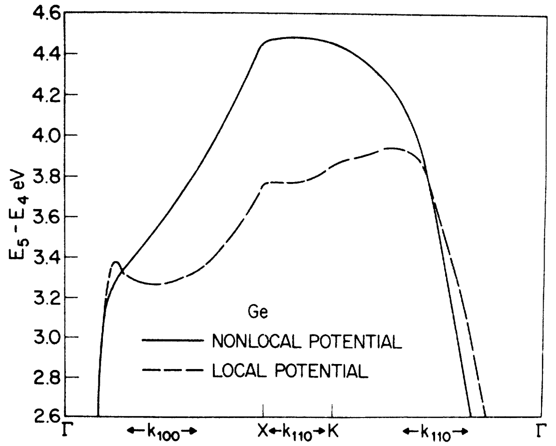

FIG. 2. Plot similar to Fig. 1, except with $\vec{k}$ along ⟨100⟩ or ⟨110⟩ symmetry axes. Again the nonlocal $E(\vec{k})$ is much smoother than the local $E(\vec{k})$, although the curves are otherwise quite similar. As a result of the smoothing process, the critical point near Γ in $E_l(\vec{k})$ is eliminated from $E_{nl}(\vec{k})$, while the critical points near X and K that were separated by 0.2 eV in $E_l(\vec{k})$ become a single flat maximum in $E_{nl}(\vec{k})$, essentially degenerate to within 0.02 eV, which is less than the uncertainty in these values associated with convergence of the wave functions. The latter behavior is also what is found in ER data (see text).

The important changes in critical point topology are for $E(\vec{k}) = E_5(\vec{k}) - E_4(\vec{k})$, i.e., the difference in energy of the lowest conduction and highest valence bands. This difference is plotted for the ⟨111⟩ direction between Γ and L in Fig. 1, and for the ⟨100⟩ and ⟨110⟩ symmetry axes near X in Fig. 2. For comparison the results obtained from Cohen and Bergstresser's local pseudopotential[5] are also shown. In both cases the effect of the nonlocal pseudopotential is to reduce or remove an extra oscillation in $E(\vec{k})$, thereby eliminating a critical point along Λ, and bringing the two critical points near X very close together in energy. This sharpens the E_1 absorption edge near 2 eV quite dramatically, giving it almost a step-function character, and places the $E(X)$ energy almost exactly at that of the E_2 peak.

The changes shown in Figs. 1 and 2 are small. Nevertheless, previous workers have attached significance to the extra critical points present in the energy bands based on local pseudopotentials. Once the energy levels at Γ, X, and L were fixed, slightly different local-pseudopotential parameters were found to give essentially the same critical-point topology. The flattening of $E(\vec{k})$ produced by the nonlocal perturbation term shows that this term leads to greater interactions of these two bands with other bands (especially band 5 with band 6) for $\vec{k}$ along symmetry lines and away from symmetry points. The local pseudopotential removes accidental ("crossing") degeneracies which would be present in a free-electron model, and the nonlocal term apparently does so somewhat more strongly. The effect is small (~0.1–0.2 eV) but significant both in the present calculations and in the interpretation of experimental line shapes.

The effect of the nonlocal term on the E_1 peak is particularly gratifying. The flattening of $E(\vec{k}) = E_5(\vec{k}) - E_4(\vec{k})$ along $\vec{k} = \Lambda$ shown in Fig. 1 clearly gives the E_1 edge a two-dimensional character. Analysis of high-field electroreflectance (ER) data suggested[15] that to within about 0.05 eV the flat region extended about $\beta = 0.8$ [actually 1.6 (!)[15]] of the distance along Λ from L to Γ. This high-field analysis was later criticized[16] and supplemented by a low-field analysis, with the effects of lifetime broadening and final-state Coulomb interactions treated more accurately. By accident the low-field analysis, which is accurate to about 0.02 eV, also yielded a (rough) value of β near 0.8.

It would be unrealistic to claim that the topology of the $\Lambda_1 - \Lambda_3$ energy difference is accurately predicted by the present calculation. However, our parameters were determined by the symmetry-point energies, without regard to the presence or absence of an additional critical point along Λ. In Fig. 1 we have drawn as dotted lines estimates of the $E(k)$ curves compatible with both the high-field[15] and low-field electroreflectance data.[16] It can be seen that the curve for $E_{nl}(\vec{k})$ derived from the nonlocal potential is much more consistent with experiment than the curve $E_l(k)$ based on the older local pseudopotential.[5] The nonlocal curve gives a value for β of about 0.5, which is somewhat less than the value of 0.8 that ER data suggest. However, in all likelihood the use of a Coulomb (rather than contact) interaction to describe final-state attractions would sharpen the absorption edge, leading to a smaller value of β. Considering the uncertainties involved in the theoretical calculation, the agreement with experiment is entirely satisfactory.

We note here that thermoreflectance (TR) data have been interpreted[17] as placing $E(L)$ below $E(\Lambda)$ by 0.03 eV. However, the TR oscillations are about four times broader than the (intrinsic) width of the low-field ER oscillations, which do not exhibit similar fine structure. It appears, therefore, that great weight should not be attached to the TR data, and that the conclusion of the ER data, that there is no evidence for an additional critical point in $E(k)$ between L and Γ, should be allowed to stand.

In the neighborhood of the X and K points, along the symmetry lines Δ and Σ, the energy band $E_l(\vec{k})$ derived from the local pseudopotential exhibits two critical points, one near X and one near K, separated by 0.2 eV. By contrast, in $E_{nl}(k)$ these two critical points are degenerate within 0.02 eV, and hence would appear in ER data as a single critical point. This topology is the one found experimentally.[18] We repeat that details of this kind are a byproduct of the calculation, and were not considered in fitting the parameters to the principal energy gaps listed in Tables I and II.

TABLE I. Principal energy gaps in Ge.

	CB[a]	Experiment	Nonlocal potential	Equivalent local
$\Gamma_{25'} \rightarrow \Gamma_{2'}(E_0)$	1.15	0.99[b]	0.99	3.17
$\Gamma_{25'} \rightarrow \Gamma_{15}(E_0')$	3.54	3.23[b]	3.22	3.97
$L_{3'v} \rightarrow L_{1c}(E_1)$	2.05	2.34[b]	2.33	3.25
$L_{3'v} \rightarrow L_{3c}(E_1')$	5.35	5.80[c,d]	5.82	5.73
$X_{4v} \rightarrow X_{1c}(E_2)$	3.77	4.50[b,d]	4.48	4.49
$\Sigma_{2v} \rightarrow \Sigma_{3c}[E_2(\Sigma)]$	3.86	4.50[b]	4.46	4.63
$\Gamma_{25'} \rightarrow L_{1c}$	0.97	0.84[e]	0.86	2.26
$\Gamma_{25'} \rightarrow X_{1c}$	1.21	1.26[f]	1.24	2.11
$\Gamma_{25'} \rightarrow \Delta_{1c}^{min}$	1.07	1.06[g]	1.04	1.96
$\Gamma_{1v} \rightarrow \Gamma_{25'}$	11.93	12.6 ± 0.3[h,i]	12.55	11.30
$L_{2'v} \rightarrow \Gamma_{25'}$	9.91	10.6 ± 0.4[h,i]	10.42	9.29
$L_{1v} \rightarrow \Gamma_{25'}$	6.93	7.7 ± 0.3[h,i]	7.52	6.35
$\Sigma_{1min} \rightarrow \Gamma_{25'}$	3.85	4.5 ± 0.3[h,i]	4.57	3.51
$L_{3'v} \rightarrow \Gamma_{25'}$	1.07	1.4 ± 0.2[i,b,e]	1.47	0.99
$X_{4v} \rightarrow \Gamma_{25'}$	2.56	2.9 ± 0.3[i]	3.23	2.38
$\Gamma_{25'} \rightarrow L_{3c}$	4.28	4.3[j]	4.35	4.73

[a] Reference 5.

[b] Reference 18.

[c] R. R. Z. Zucca and Y. R. Shen, Phys. Rev. B <u>1</u>, 2669 (1970).

[d] D. E. Aspnes (private communication).

[e] J. E. Fischer, *Proceedings of the Tenth International Conference on the Physics of Semiconductors* (MIT Press, Cambridge, Massachusetts, 1971), p. 427.

[f] F. Herman, R. L. Kortum, D. C. Kuglin, and R. A. Short, in *Quantum Theory of Atoms, Molecules and the Solid State*, edited by P. O. Löwdin (Academic, New York, 1966).

[g] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. <u>109</u>, 695 (1958).

[h] Reference 3.

[i] J. E. Rowe (unpublished).

[j] W. E. Spicer and R. C. Eden, in *Proceedings of the Ninth International Conference on Semiconductors* (Nauka, Leningrad, 1968), Vol. 1, p. 61.

IV. INTERBAND DATA

The principal source of new data is the work by Aspnes[2,16,18] using the Schottky barrier ER technique which he has developed.[2,19] This powerful technique yields simple oscillations that can be analyzed rigorously in terms of low-field theoretical expressions for the line shape. It automatically removes from the problem certain ambiguities which often arise in attempting to extract critical-point energies from reflectance data, with or without the benefit of a Kramers-Kronig transformation of $R(\omega)$ to yield $\epsilon_2(\omega)$. Finally, the data are taken at low temperatures ($T \sim 10$ °K). Other sources of data are indicated in Tables I and II for indirect energy gaps. The discussion of the data for the E_1' edge in GaAs, which lies outside the spectral range studies by Aspnes, is based on thermo-

TABLE II. Principal energy gaps in GaAs.

	CB[a]	Experiment	Nonlocal potential	Equivalent local
$\Gamma_{15v}\rightarrow\Gamma_{1c}(E_0)$	1.42	1.63[b]	1.64	3.80
$\Gamma_{15v}\rightarrow\Gamma_{15c}(E_0')$	4.54	4.71[b]	4.69	5.09
$L_{3'v}\rightarrow L_{1c}(E_1)$	2.62	3.16[b]	3.18	4.04
$L_{3'v}\rightarrow L_{3c}(E_1')$	5.94	6.60[c]	6.74	6.46
$X_{5v}\rightarrow X_{1c}(E_2)$	4.06	4.97[b]	4.96	4.96
$X_{5v}\rightarrow X_{3c}(E_2')$	4.37	5.38[b]	5.34	5.14
$\Sigma_{2v}\rightarrow\Sigma_{3c}[E_2(\Sigma)]$	4.32	5.14[b]	5.13	5.23
$\Delta_{5v}\rightarrow\Delta_{1c}$	4.24	4.62[b]	4.62	5.01
$\Gamma_{15v}\rightarrow X_{1c}$	1.79	2.06[d]	2.12	2.91
$\Gamma_{15v}\rightarrow L_{1c}$	1.72	⋯	1.97	3.24
$\Gamma_{1v}\rightarrow\Gamma_{15v}$	12.25	12.9 ± 0.6[e]	12.63	11.32
$X_{3v}\rightarrow\Gamma_{15}$	6.14	6.8 ± 0.3[e]	6.50	5.42
$\Sigma_{1\min}\rightarrow\Gamma_{15v}$	3.60	4.1 ± 0.2[e]	4.20	3.14
$L_{3'v}\rightarrow\Gamma_{15v}$	0.90	1.1 ± 0.3[e]	1.21	0.80
$X_{1v}\rightarrow\Gamma_{15v}$	10.18	10.4[e]	10.36	9.11

[a] Reference 5.

[b] Reference 2.

[c] Reference 21.

[d] I. Balslev, Phys. Rev. 173, 762 (1968).

[e] Reference 3.

reflectance data[20] and is given in a separate paper.[21]

Comparison with the experimental data is given in Tables I and II. The agreement is extraordinarily good[8] for both Ge and GaAs. In the case of Ge only four parameters are adjusted (V_3, V_8, V_{11}, and A_2), and the fit is good on ten energy gaps, to within a few hundredths of an eV. The differences from experiment in the local pseudopotential model were typically a few tenths of an eV. Moreover, the deeper valence band levels are given by the nonlocal potential in better agreement with photoemission data, although again no effort was made to adjust the parameters to deal with this data. At the present stage of development, we regard the energies of the deeper valence band states as a by-product of the calculation, to be used as an aid in interpreting photoemission data, bearing in mind the problems of interpretation associated with the latter.

V. DISCUSSION OF PARAMETERS

The format used here to present the parameters of the calculation is the same as in Ref. 8, except that here only the $l=2$ nonlocal term differs from zero; it was shown[8] that other nonlocal terms do not improve the fit to experiment. We contrast the old local pseudopotential form factors for $G^2 \leqslant 11$ with those of our nonlocal potential and with those of an equivalent local pseudopotential derived from the nonlocal one following the conventional prescription.[8]

The parameters for Ge are shown in Table III. Note that $V_{\text{loc}}^{\text{equiv}}$ (8, 11) is close to V_{mod} (8, 11), the latter being based on free ion-term values. Indeed $V_{\text{loc}}^{\text{equiv}}$ (8, 11) is closer to V_{mod} (8, 11) than the older local pseudopotential[5] values V_{CB} (8, 11). On the other hand, $|V_{\text{loc}}^{\text{equiv}}(3)|$ is now greater than $|V_{\text{mod}}(3)|$ by 0.05 Ry, whereas the difference between the latter and V_{CB} (3) was only 0.04 Ry.

The value of $V_{\text{mod}}(q)$ is essentially that of the free ion $V_{\text{ion}}(q)$, screened by the free-electron dielectric function $\epsilon_f(q)$ appropriate to a nearly-free-electron metal; thus

$$V_{\text{mod}}(q) = V_{\text{ion}}(q)/\epsilon_f(q) . \tag{8}$$

One expects, of course, that in a semiconductor $\epsilon_s(q) < \epsilon_f(q)$; in particular, $\epsilon_s(0) = 16$ in Ge, whereas $\epsilon_f(q) \propto q^{-2}$ as $q \rightarrow 0$. The value $G^2 = 3$ corresponds to $q/2k_F = G/2k_F = 0.55$. Using an interpolation formula for $\epsilon_s(q)$, one can then attempt to allow for reduced screening of ionic potentials in semiconductors. The value for

$$\delta V(0.55k_F) = V_{\text{ion}}(0.55k_F) \times \{[\epsilon_s(0.55k_F)]^{-1} - [\epsilon_f(0.55k_F)]^{-1}\} \tag{9}$$

obtained in this way[22] is 0.045 Ry, which seems to be in good agreement with the above values. However, there is another term (whose presence is necessary because of the requirement of charge neutrality, and which has been physically interpreted as being associated with bond charges) which reduces this value by 0.010 Ry, giving a shift of only 0.035 Ry. This does not agree so well with the shift of 0.050 Ry obtained here. It is likely that the dielectric screening approach must be handled more accurately, and must include a more delicate treatment of exchange and correlation effects (which would tend to increase δV). In any event, the trends discussed here for Ge may well be important in analyzing the electronic structure of more complicated tetrahedrally coordinated semiconductors.

The parameters for GaAs, which are shown in Table IV, provide an immediate test for this conjecture. For V_8^s, V_{11}^s, and V_{11}^a, $V_{\text{equiv}}^{\text{loc}}$ is again very close to V_{mod}, much closer than was V_{CB}. On the other hand, for V_4^a one has $V_{\text{equiv}}^{\text{loc}}$ 16% greater than V_{mod}, and for V_3^a it is 22% greater. This is exactly the trend observed for V_3^s, and as expected the ef-

TABLE III. Pseudopotential form factors for Ge at various momenta G^2 [in units of $(2\pi/a)^2$ and Ry/atom]. First line: crystalline semiempirical local values of Ref. 5. Second line: atomic model potential (Ref. 12). Third line: equivalent local values derived from the present nonlocal pseudopotential. The local part of the present potential is given in line four. The nonlocal strength parameters for the d term are also given in line four. The parameter R_2 is given in Å. The sizes of the basis sets used in the calculation were selected with the same energy cutoffs as those used in Refs. 5 and 14.

	V_3^s	V_8^s	V_{11}^s	A_2	R_2
V_{CB}	−0.230	0.010	0.060	⋯	⋯
V_{mod}	−0.190	0.030	0.070	⋯	⋯
$V_{\text{loc}}^{\text{equiv}}$	−0.240	0.032	0.078	⋯	⋯
V_{nonl}	−0.223	0.029	0.050	0.582	1.225

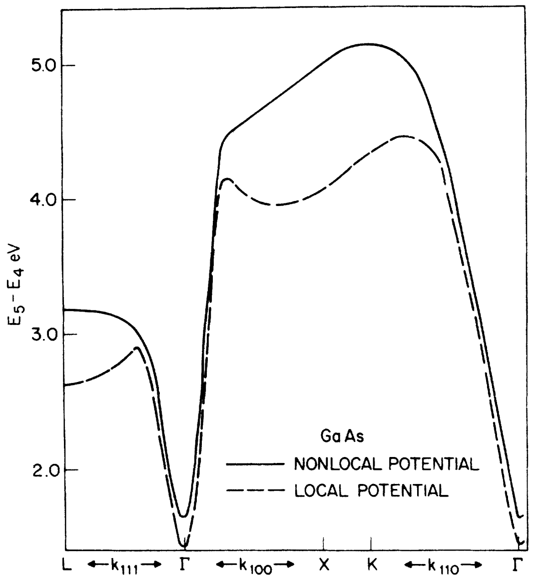

FIG. 3. Plot similar to Figs. 1 and 2 for GaAs. Note again the smoothing effect of the nonlocal term in the pseudopotential.

fect is larger for V_3^s than it is for V_4^a. For V_3^s in GaAs the shift is 30%, compared to 26% for V_3 in Ge.

We are aware, of course, that our fitting procedure is not unique, and that these numbers should be regarded as circumstantial evidence for a quantitative trend, and not as proof of a rigorous mathematical resolution of the problem of many-body contributions to the effective one-electron potential in partially ionic semiconductors. Nevertheless, the internal consistency of these numbers is remarkable, and they should prove to be a useful guide in studying the electronic structure, e.g., of chalcopyrite semiconductors.

The radius R_2 and well height ($A_2 > 0$) of the nonlocal term in Ge were chosen so that the radius was equal to half the interatomic distance. In GaAs, $R_{\rm Ga} + R_{\rm As}$ is equal to the interatomic distance, and the ratio $R_{\rm Ga}/R_{\rm As}$ is equal to $Z_{\rm As}/Z_{\rm Ga}$ where Z_A is the effective charge of element A seen by the d electrons in the last filled d shell, and Z_A is computed using Slater's rules.[23] However, with suitable choices of $A_2({\rm Ga})$ and $A_2({\rm As})$, other choices of $R_{\rm Ga}$ and $R_{\rm As}$ would give an equally good fit to the experimental data. The smoothing effect of the nonlocal potential on $E_5 - E_4$ is shown for GaAs in Fig. 3.

Perhaps the most interesting feature of the nonlocal parameters is that in all cases studied the nonlocal contribution to $V_{G^2}^a$ is about ten times smaller than the nonlocal contribution to $V_{G^2}^s$. (This contribution is shown in Table IV as the difference between $V_{\rm loc}^{\rm equiv}$ and $V_{\rm nonl}$.) This means that the nonlocal d effect on the energy bands of GaAs is almost the same as the d effect on the energy bands of Ge. This conclusion has also been reached previously by Van Vechten using the dielectric method.[24]

After this manuscript was completed, we received a preprint of a nonlocal pseudopotential calculation for Ge by Chelikowsky and Cohen.[25] They reach conclusions quite similar to ours, especially as regards the plateau character of the energy-band difference responsible for the E_2 peak. However, as regards the E_1 peak, we consider the electroreflectance data as more definitive, and hence we place greater stress on the agreement between theory and experiment shown in our Fig. 1.

Another comment which may be added is based on nonlocal corrections in nearly-free-electron metals, as studied by Weaire.[26] While the applicability of these corrections over the wide energy range considered here is doubtful, they do enable us to make estimates of the degree of ambiguity involved in relating the parameters determined here to model-potential form factors.[12]

Weaire calculates two corrections to the nearly-free-electron Hamiltonian, denoted by m_K and m_E, which represent corrections to the kinetic energy and the eigenvalue E. The product $m_K m_E$ is nearly unity, and one can therefore regard m_E as a scaling factor which replaces the model potential V_M by V_M / m_E. The calculated value for m_E in Ge is 0.94. Comparing lines 2 and 3 of Table III, we see that with the semiconductor screening correction mentioned above

TABLE IV. Pseudopotential form factors for GaAs at various momenta G^2 [in units of $(2\pi/a)^2$ and Ry/atom]. First line: crystalline semiempirical local values of Ref. 5. Second line: atomic model potential (Ref. 12). Third line: equivalent local values derived from the present nonlocal pseudopotential. The local part of the present potential is given in line four. The nonlocal strength parameters for the d term are also given in line four. The parameters $R_{\rm Ga}$ and $R_{\rm As}$ are given in Å. The sizes of the basis sets used in the calculation were selected with the same energy cutoffs as those used in Refs. 5 and 14.

	V_3^2	V_8^s	V_{11}^s	V_3^a	V_4^a	V_{11}^a	$A_{\rm Ga}$	$R_{\rm Ga}$	$A_{\rm As}$	$R_{\rm As}$
$V_{\rm CB}$	−0.230	0.010	0.060	0.070	0.050	0.010				
$V_{\rm mod}$	−0.185	0.036	0.097	0.058	0.049	−0.013				
$V_{\rm loc}^{\rm equiv}$	−0.240	0.032	0.082	0.071	0.057	−0.006				
$V_{\rm nonl}$	−0.233	0.029	0.050	0.071	0.058	−0.009	0.446	1.332	1.096	1.110

for V_3^s, the agreement between V_M/m_E and our parameters is better than that achieved by V_M for $G^2 = 3$, 8, and 11.

We have benefited substantially from many conversations with Aspnes.

APPENDIX A

In Sec. I it was stated that replacing $p^2/2m$ in the Hamiltonian by $p^2/2m^*$ is an unsatisfactory approach to describing nonlocal corrections to the local pseudopotential energy bands.

The experimental values for valence band energies systematically indicate[8] that in Ge the valence band is wider than is predicted by a local pseudopotential. Because the valence bandwidth is primarily determined by the kinetic energy, this requires that one choose for m^* a value such that

$$m - m^* > 0 \ . \tag{A1}$$

For valence-conduction band energy differences again the experimental energy differences are *greater* than are given by the local pseudopotential.[8] However, in this case we are dealing with energy differences between states which were degenerate in the free-electron approximation. Thus the role of the kinetic energy in affecting these energy differences is not the same as its (primary) role in determining the valence bandwidth.

To see what the role of the kinetic energy $T^* = p^2/2m^*$ is compared to that of $T = p^2/2m$, one can recall the simple expression[27] for the $X_{1c} - X_{4v}$ energy given by second-order perturbation theory

$$E(X_{1c}) - E(X_{4v}) = 2V_{220} + 2V_{111}^2/\Delta T \ , \tag{A2}$$

where ΔT is given in terms of kinetic energies by

$$\Delta T = T([110]) - T([001]) \ . \tag{A3}$$

With appropriate values of V_{220} and V_{111}, the second-order term in (A2) dominates the linear term.

If we now replace ΔT in (A2) by ΔT^*, then we find that the value of m^* required to increase the conduction-valence band energy gap satisfies

$$m^* - m > 0 \ , \tag{A4}$$

in direct contradiction to (A1). Thus the replacement of T by T^* is an unsatisfactory approach.

It might be thought that an argument based on the relation (A2) is special, and does not apply to other symmetry points in the Brillouin zone. At X the second-order term is associated with the interaction between X_{1c} ([011] plane waves in the free-electron approximation) and X_{1v} ([100] plane waves). However, the gap at L is similarly affected by the interaction between L_{1c} $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$ and L_{1v} $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while at Γ the important interaction is between $\Gamma_{25'}$ [111] and $\Gamma_{25'}$ [200]. In each case a formula similar to (A2) obtains. Specifically, the results are

$$E(L_{1c}) - E(L_{3'v}) \cong E_1 = 3V_8 + \sqrt{2}^{\,-1}(V_3 + 2V_{11}) + (3/8\Delta T)(2V_3^2 - 3V_{11}^2 - 6V_3V_{11}) \ , \tag{A5}$$

$$E(\Gamma_{2'c}) - E(\Gamma_{25'v}) = E_0 = V_8 + \tfrac{1}{2}\{[(\Delta T)^2 + (8\Delta_-^2)]^{1/2} - [(\Delta T)^2 + 24\Delta_+^2]^{1/2}\} \tag{A6}$$

$$\Delta_\pm = V_3 \pm V_{11} \ . \tag{A7}$$

Because $V_3 \gg V_{11}$, the dependence of E_1 in Eq. (A5) on ΔT is qualitatively similar to that of E_2, as described by Eq. (A2). The second term in Eq. (A6) dominates the first one, again giving a dependence on ΔT of E_0 similar to that found for E_1 and E_2.

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