power in the kilowatt range. All the above data are for frequencies in the 10- to 140-Mc/sec range and for electrode separations from 1 to 10 cm.

Finally, the Herlin and Brown[9] data show that multipacting can be the dominant microwave breakdown mechanism at pressures below the mean free path limit of the diffusion mechanism.[10] Their breakdown data for 3125 Mc/sec (Fig. 2 in reference 9) indicate that at a pressure of about 0.1 mm Hg in air the field strength *vs* pressure curves tend to level off to steady values. From Herlin and Brown's curves we have determined these values as listed in column 3 of Table I. The electrode separations and corresponding fd values are listed in columns 1 and 2, respectively. The breakdown V values in peak volts in column 4 are obtained from column 1 and the rms E values of column 3. The kinetic-theory mean free path for electrons in air at this pressure is about 0.5 cm, longer than any of the electrode separations used. The V and fd values from this table are plotted in Fig. 4. The three points appear to correspond to $\frac{1}{2}$-, $\frac{3}{2}$-, and $\frac{5}{2}$-cycle multipacting. The emergence of multipacting as the dominant mechanism at sufficiently low pressures is similarly evident in other microwave breakdown data.

TABLE I. Low-pressure extrapolation of microwave breakdown data showing multipacting characteristics (adapted from Herlin and Brown[a]).

Electrode separation d, cm	fd, Mc-cm/sec	Breakdown E, rms volts/cm	Breakdown V, peak volts
0.0635	200	1800	160
0.157	490	1800	400
0.318	990	1500	670

[a] See reference 9.

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[9] M. A. Herlin and S. C. Brown, Phys. Rev. 74, 291 (1948).

[10] S. C. Brown and A. D. MacDonald, Phys. Rev. 76, 1629 (1949).

PHYSICAL REVIEW VOLUME 112, NUMBER 3 NOVEMBER 1, 1958

Energy-Band Interpolation Scheme Based on a Pseudopotential

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(Received July 14, 1958)

In this paper an interpolation scheme is developed that depends on only a few parameters. This is done by observing that the effective potential for electrons near the Fermi level can be split into two parts, the part due to the core, and the part due to the other valence electrons. It is assumed that for semiconductors the relative effect of the core is small, so that it can be replaced by an effective repulsive potential. In this way two-parameter pseudopotentials are constructed for diamond and Si that give good agreement with orthogonalized plane wave calculations and experiment at special points of the Brillouin zone, and also yield reasonable results for the bands at other points of the zone. A by-product of the calculations is the discovery of an error in the model for the valence bands of Si near the center of the zone proposed by Dresselhaus. A compromise model is proposed in good agreement with theory and experiment. Good results are obtained for Ge with a three-parameter pseudopotential. Finally, the many experimental facts that have been deduced about the band structures of Si and Ge are augmented by the results of the pseudopotential calculations to yield fairly accurate ($\delta E \lesssim 0.05$ ry) sketches of the energy bands of these crystals along the [100] and [111] directions in the neighborhood of the energy gap.

1. INTRODUCTION

THE complete determination of the electronic energy bands of a solid requires knowledge of the energy E in the ith branch, for all i of interest, and for all wave vectors $\mathbf{k}$ of the Brillouin zone. In practice most calculations have determined $E_i(\mathbf{k})$ only for wave vectors $\mathbf{k}$ possessing a sufficiently high symmetry. In such cases group theory[1,2] can be used to reduce the order of the secular equation. It has been found[2] that in semiconductors even the points of highest symmetry, such as $\mathbf{k}=0$, require the solution of approximately 10×10 secular equations. Thus a convergent solution at other points of the Brillouin zone is not easily obtained. In addition, the $E(\mathbf{k})$ curves are known[1] to be smooth functions of $\mathbf{k}$, so that if one knew $E_i(\mathbf{k})$ at two symmetry points, one would be tempted to interpolate between them, at least along the symmetry line connecting them.

For these reasons Slater and Koster[3] proposed an interpolation scheme based on the tight-binding approximation. They pointed out that if the various overlap integrals occurring in the tight-binding formalism are regarded as disposable parameters, the matrix elements of the secular equation will have, as a function of $\mathbf{k}$, a simple analytic form. The parameters are then determined by fitting energy values determined by cellular or orthogonalized plane wave treatments at symmetry points. While this viewpoint is appropriate

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[1] Bouckaert, Smoluchowski, and Winger, Phys. Rev. 50, 58 (1936).

[2] F. Herman, Phys. Rev. 88, 1210 (1952); 93, 1214 (1954).

[3] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

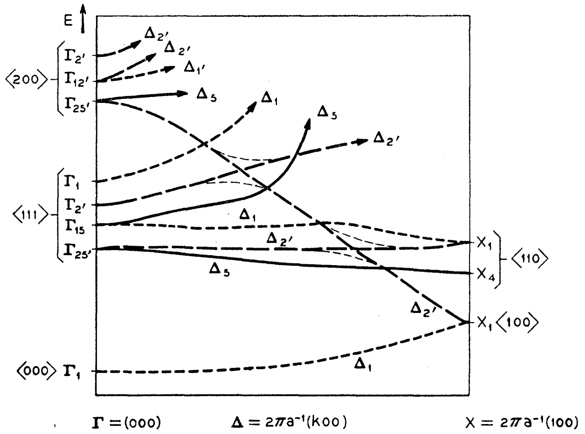

FIG. 1. A schematic diagram of the energy bands of a diamond-type lattice in the nearly-free-electron limit along the [100] direction. For the sake of clarity, the separations of the bracketed bands are greatly exaggerated. The notation used for the irreducible representations in this and the subsequent figures is that of Herring.[6]

to *d* bands whose atomic functions have a small overlap, it is not appropriate, e.g., to the conduction bands of the group IV semiconductors. In this case the wave functions are more nearly like plane waves, and for this reason Allen[4] proposed an alternate interpolation scheme based on Herring's orthogonalized plane-wave formalism.[5] Allen's approach was similar to Slater and Koster's with regard to core orbitals, but it introduced the first few Fourier coefficients of the crystal potential also as disposable parameters. The resulting number of parameters was about the same as Slater and Koster's, and was susceptible to reduction by a simplified treatment of core orbitals. The method, however, still contained orthogonality terms whose *k* dependence complicated the form of the solution.

For these reasons we were led to consider modifications of the orthogonalized plane wave formalism that would convert it into a simple interpolation scheme. The basic ideas that dictated the formalism that was finally selected will now be discussed.

2. GENERAL CONSIDERATIONS REGARDING INTERPOLATION SCHEMES

Before exploring the orthogonalized plane wave formalism further with a view to using it as an interpolation scheme, we find it convenient to consider the approximation of nearly free electrons. The results that would be obtained in this approximation for a diamond lattice along the [100] direction are shown schematically in Fig. 1.[6] In the free-electron approximation ($V=0$) the various representations that are grouped by brackets would be degenerate, as would a number of the energy curves along Δ. The first-order effect of V is to separate representations of different symmetry. In second order, representations of the same symmetry that happen to cross are separated, as is indicated by the dotted lines in Fig. 1.

Thus when we seek to construct the actual energy bands when V is not small, two different kinds of results must be obtained: (1) We must obtain the quantitative *order* of the energy levels, and (2) we must obtain the *shape* of each band, as a function of $\mathbf{k}$. The former result must presumably be obtained by detailed calculations at the symmetry points, while the latter results are to be obtained from the interpolation scheme. Thus, it is not actually necessary that the interpolation scheme reproduce all the term values that have been calculated. What is more desirable is that the scheme depend on a small number of parameters but reproduce a large number of term values approximately. If this is the case we may be satisfied concerning the physical validity of the method, and have considerable confidence in the band shapes it predicts. These shapes may then be used to interpolate between the term values obtained more accurately from other calculations, or from experiment. Indeed, if the interpolation scheme can be made to depend on a sufficiently small number of parameters, these may be determined directly from experiment, and the scheme then enables one to deduce other features of the band structure of interest.

Another point to be emphasized in this connection is that even at symmetry points the term values that are obtained in detailed calculations may not be fully convergent. Thus exact agreement, obtained by using a large number of parameters, is not especially significant. Indeed, one desirable feature of the interpolation scheme is that it yield values in better agreement with experiment than those obtained from only partially convergent calculations. In this sense the scheme can provide a "bridge" between the results of experiment and calculations of band structure based on first principles. Since an increasingly detailed picture of various parts of the bands is being obtained experimentally, a simple scheme based on a few parameters that correlates the experimental information should be most welcome. As an example of this approach, in Sec. 5 a two-parameter model for Si is constructed that yields good agreement with eight experimental values; similar results are also obtained for Ge in Sec. 6. Finally, in Sec. 7 these results are collected and the energy bands of both crystals are sketched with considerable accuracy in the [100] and [111] directions by slightly modifying the earlier results to bring them into complete agreement with experiment.

3. A PSEUDOPOTENTIAL INTERPOLATION SCHEME

From the discussion of the last section it is clear that the best justification for an interpolation scheme

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[4] L. C. Allen, Phys. Rev. **98**, 993 (1955).

[5] C. Herring, Phys. Rev. **57**, 1169 (1940).

[6] The notation used for the various symmetry points is the same as that of reference 1. The notation for the various irreducible representations of the diamond lattice is the same as that of C. Herring, J. Franklin Inst. **233**, 525 (1942).

lies in the results that can be obtained from it. Nevertheless, in this section we shall describe our scheme and present some physical arguments which suggest that it might be successful. In practice it turns out to be much more successful than the arguments would imply; thus, the arguments should be understood more nearly as an attempt to explain the results rather than to justify them.

Our method is based on a pseudopotential, which is constructed in such a way that it includes the effects of the core. Thus, the lowest states of the pseudopotential are the lowest states of the valence band, which we presume are well separated from the core levels. For the sake of simplicity we direct our attention now to semiconductors; the discussion would also apply to metals, if suitably modified.

We now define our pseudopotential by demanding that it give a good fit for the energy bands of interest, which are the bands near the energy gap. The entire effect of the core, through orthogonality corrections as well as through its contributions to the crystal potential, is to be included in the pseudopotential. Moreover, in practice it proves necessary to truncate the Fourier expansions of eigenfunctions at a small number of plane waves. It is intended that the pseudopotential should include the effects of interactions with higher plane waves with the states of interest in an approximate way. We now discuss the possibility of achieving these objectives.

That core effects might be represented by a repulsive contribution to a pseudopotential was first recognized by Hellman,[7] who applied the method to molecules[7] and metals.[8] As Herring has observed,[9] his approximation can be justified formally by observing that the orthogonalization terms in the orthogonalized plane wave formalism[5] have a repulsive character. The appearance of the expression $(E_{nl}-E)$ in these terms causes no difficulty, since E can be approximated by any constant value chosen to fit the region of interest; the error should be small since the core levels E_{nl} are so far away from the region of interest. Symmetry effects (a valence electron in an s state such as Γ_1 experiences orthogonality corrections only from s levels in the core) can presumably be included approximately by using operators measuring the relative $s, p, d, \ldots$ character of the various plane waves. If one is concerned primarily with s and p functions and mixtures of them, the problem is considerably simplified. Moreover, the effect of truncation (which is discussed in more detail below) is to reduce the importance of the higher Fourier coefficients in the calculation.

Since the core is small, we find it plausible that its effect on the energy bands can be represented approximately by a pseudopotential. It is less clear how the crystal potential itself is to be represented. The contributions of the core to the crystal potential can easily be included along with its repulsive effects. The difficult part is the contribution of the valence electrons. The latter part of the potential, however, may be expected to be slowly varying, so that only its first few Fourier coefficients should be appreciable. We may also take these as disposable parameters; thus, in the spirit of Ewald, we split the crystal potential into two parts, one of which is large only near the origin of physical space, the other large only near the origin of k space.

Finally, we must consider the size of the secular determinants we shall solve, and the effect of limiting them (truncating) on the results. It was originally hoped that including all the states in the valence band and an equal breadth in energy in the conduction band would be sufficient. This did not prove to be the case; instead it was necessary to adopt the criterion that enough states were included so that each state of interest near the energy gap interacted with at least one higher state (of the same symmetry).

Even in this case we shall presumably include considerably fewer states than have been included in the more accurate calculations at the symmetry points; this in fact was one of the original objectives. The question now arises, to which term values shall we fit our parameters? One might use the best values, obtained with as many states as possible, or one might fit to the results obtained using a realistic potential and the same number of states. Since different representations converge at different rates (especially the p states as compared to the s states; see Herman[2] and Woodruff[10]), this is a significant point. Our view is the following: if values have been obtained which appear to have converged reasonably well, these are the ones that should be used, even if they have been obtained by including more states than we use in the pseudopotential calculation. The justification for this is that different rates of convergence appear to be due chiefly to different atomic symmetries, and we have already attempted to include such effects in our treatment of the repulsive effect of the core, so that it is consistent to extend the earlier treatment to this point as well.

The introduction of a pseudopotential to represent the repulsive effect of the core can also be justified by a Thomas-Fermi treatment of the core. Thus Gombás[11] and his associates have independently given a semiclassical treatment that is in many respects parallel to that of Hellman. In particular Szepfalusy[12] has shown that the orthogonality terms can be replaced by a linear operator which has a semiclassical interpretation in the statistical theory as a repulsive potential. We

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[7] H. Hellmann, J. Chem. Phys. **3**, 61 (1935); Acta Physicochim. U.R.S.S. **1**, 913 (1935); Acta Physicochim. U.R.S.S. **4**, 225 (1936).

[8] H. Hellmann and W. Kassatotschkin, J. Chem. Phys. **4**, 234 (1936); Acta Physicochim. U.R.S.S. **5**, 23 (1936).

[9] C. Herring, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 81.

[10] T. O. Woodruff, Phys. Rev. **103**, 1159 (1956).

[11] P. Gombás, *Die Statistische Theorie des Atoms und Ihre Anwendung* (Springer-Verlag, Vienna, 1949), p. 150.

[12] C. Szepfalusy, Acta Phys. Acad. Sci. Hung. **5**, 325 (1955).

are not concerned here in such detail with the core since the effect of truncating the secular equations is to reduce the importance of the core, and to introduce "nonphysical" contributions to the pseudopotential in order to compensate for the different rates of convergence of *s* and *p* states. It is sufficient for our purposes that an approximate treatment of the effects of the core can be given by the pseudopotential method.

4. APPLICATION TO DIAMOND

After this long discussion it may not be surprising that the pseudopotential to be used for group IV semiconductors is quite simple. From Herman's table of the Fourier coefficients of the crystal potential of diamond[13] it is seen that the valence electrons make an appreciable contribution only to V_{111}. (Their next largest contribution, to V_{220}, is some 20 times smaller.) Thus the remaining coefficients belong to the core, so that they should decrease gradually as a function of k. (This is actually the case, as may also be seen from Herman's table.) For our purpose, it is sufficient to take the remaining coefficients equal to a single constant. This is a consistent procedure as long as we truncate the secular equation and restrict ourselves to a limited number of plane waves. It should be remarked that our parameters refer to the potential of a single atom. If there is more than one atom of the same kind per unit cell we introduce the usual form factor [see Eq. (4.3) below, which can be compared with Eqs. (3.7) and (3.8) of reference 2]. Finally the zero of energy is fixed by a suitable choice of V_{000}.

Thus we obtain our energy bands from the following one-electron Hamiltonian:

$$H=p^2/2m+V_p(r), \tag{4.1}$$

where $V_p(r)$ is the pseudopotential. Since V_p is a local space potential, we have assumed that the effects of exchange and correlation can be approximated by the introduction of effective local exchange and correlation potentials. In practice this assumption is made for almost all band calculations. The pseudopotential can now be expanded in a Fourier series

$$V_p(r)=\sum_{\mathbf{K}} V_K e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{4.2}$$

where our prescription for the Fourier coefficients is

$$\begin{aligned} V_{000}=\alpha, \quad V_{\langle 111\rangle}&=V_1\cos[8^{-1}(K_1+K_2+K_3)a], \\ V_{\mathbf{K}}&=\gamma\cos[8^{-1}(K_1+K_2+K_3)a], \\ &\qquad \mathbf{K}\neq 0,\ \langle 111\rangle, \end{aligned} \tag{4.3}$$

where $\mathbf{K}$ denotes a reciprocal lattice vector, and $\langle 111\rangle$ denotes any of the reciprocal lattice vectors of the form $(\pm 2\pi/a,\pm 2\pi/a,\pm 2\pi/a)$. Thus we have introduced three disposable parameters: α, γ, and V_1. This is the form of pseudopotential used for diamond and silicon; if necessary, it can be generalized by taking more of the lower Fourier coefficients as parameters. This is done for germanium, where our scheme requires four parameters. By contrast Slater and Koster's scheme for diamond[3] used eleven parameters.

TABLE I. Comparison of term values for diamond obtained by Herman[a,b] in an orthogonalized plane wave calculation with those obtained by the three-parameter interpolation scheme described in the text. Energies are measured in rydbergs, and the notation for the various representations is that of Herring.[c] Term levels near the energy gap are in boldface.

Term	Herman	Interpolation scheme
$\Gamma_1^{(1)}$	−2.44	−3.03
$\Gamma_{25'}^{(1)}$	**−0.91**	**−0.90**
$\Gamma_{15}^{(1)}$	**−0.46**	**−0.43**
$\Gamma_{2'}^{(1)}$	**0.16**	**0.02**
$\Gamma_{12'}^{(1)}$	1.01	0.65
$\Gamma_1^{(2)}$	0.52	0.73
$X_1^{(1)}$	−1.67	−2.30
$X_4^{(1)}$	**−1.23**	**−1.46**
$X_1^{(2)}$	**−0.30**	**−0.69**
$X_3^{(1)}$		1.16
$X_4^{(2)}$		1.40
$L_1^{(1)}$	−2.33	−2.19
$L_{2'}^{(1)}$	−2.08	−2.59
$L_{3'}^{(1)}$	−1.13	**−1.10**
$L_3^{(1)}$	0.18	**−0.17**
$L_1^{(2)}$		−0.48

[a] See reference 2.
[b] See reference 11.
[c] See reference 6.

The numerical values of the parameters that are required are determined by trial and error. More explicitly, one inspects the factored secular determinants at points of maximum symmetry until one can guess good starting parameters; these are then varied slowly until a "best" set has been obtained. Apparently for the cases we have studied this leads to an essentially unique set $\{\alpha, V_1, \gamma\}$ for each crystal. Since there are many term values, all of which depend on many Fourier coefficients, the restriction to only a few parameters results in a substantial overdetermination of the problem. The foregoing physical arguments were presented to indicate that one might still expect to obtain approximate solutions; inspection of the secular equations supports this view since it shows that the interband matrix elements between the lowest conduction and highest valence bands, which are the most important ones in determining the variation of E with $\mathbf{k}$ near the energy gap, depend primarily on the first few Fourier coefficients.

We discuss the results for diamond first. They were obtained for $\alpha=-2.72$ ry, $V_1=-0.50$ ry, and $\gamma=+0.17$ ry. The results for various symmetry points are presented in Table I, which also lists Herman's best (most convergent) results. Our results in general were obtained using about 27 plane waves, which led to at most third-order secular equations at Γ ($\mathbf{k}=0$) and at most sixth-order equations along Δ [$\mathbf{k}=(k00)$].

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[13] F. Herman, Ph.D. thesis, Columbia University, 1953 (unpublished), p. 48. Available on microfilm through University Microfilms, University of Michigan, Ann Arbor, Michigan.

Herman used as many as 146 plane waves at Γ, and his largest secular equation was of order 16. He used fewer waves at X $[\mathbf{k}=2\pi a^{-1}(100)]$ and L $[\mathbf{k}=\pi a^{-1}(111)]$, so that the correct term values at those points should be lower than the ones he lists. Also his L_1 and $L_{2'}$ term values are probably in error due to a mistake in constructing the factored secular determinants for these representations.

Our pseudopotential has been constructed to yield optimal term values near the energy gap, and it is indeed these values, which are in boldface in Table I, that are of the greatest interest. The basic limitations of our scheme can be best evaluated, however, by considering the errors in the pseudopotential values for $\Gamma_1^{(1)}$, $X_1^{(1)}$, and $L_1^{(1)}$. The errors in these terms, while fairly large, are not sufficient to disturb band shapes near the energy gaps, as can be easily seen from perturbation theory. On the other hand, when one realizes that these term values differ mainly from the ones near the energy gap by kinetic energy terms it is clear that the pseudopotential correction to the free-electron values is several times that which is obtained by Herman, and so grossly in error (but not, it is to be emphasized, in a way that will spoil band shapes near the energy gap). The reason the pseudopotential yields poor values is that $\Gamma_1^{(1)}$ corresponds to an atomic 1s state, instead of to an atomic 2s state as it should.[14] To have treated these states correctly would have required more parameters and orthogonalization to the 1s level, and would very probably not have materially improved band shapes near the energy gap.

We now consider the pseudopotential results for this region in detail. From the table we see that the pseudopotential scheme yields term values that are in the right order not only at the center of the zone, but also at the edge points X and L. Moreover, the numerical agreement is qualitatively excellent at Γ, X, and L, and indeed the discrepancies, especially at X and L, are well within the limits of error due to inadequate convergence at those points. More convergent solutions would probably improve the agreement between the two sets of results.

More interesting are the results obtained along the symmetry line Δ connecting Γ and X. These are shown in Fig. 2. Term values were calculated at intervals $\Delta\mathbf{k}=0.1(2\pi a^{-1})(1,0,0)$. Sixth-order equations were solved for Δ_1, Δ_2, and Δ_5, which means that only 24 plane waves were used for each value of $\mathbf{k}$. At each $\mathbf{k}$ the lowest six symmetry types were used, and thus a discontinuous truncation is made for each type as one passes from Γ to X. (The values of $\mathbf{k}$ at which these truncations were made are the same as those shown in Fig. 5 by doubled arrows.) These discontinuities produced discontinuities in the term values near the energy gap of order 0.05 ry, and in accordance with the variational principle, at each discontinuity a smooth curve was drawn lying somewhat lower than the calculated points.

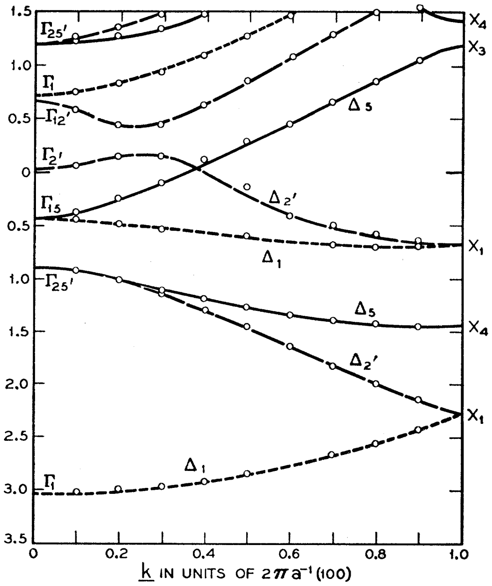

FIG. 2. The energy bands of diamond along the [100] direction, as calculated by using the interpolation scheme described in the text.

From the figure several conclusions can be drawn. The minimum in the conduction band may well occur in the [100] direction, as suggested by Herman,[13] and for $\mathbf{k}\simeq 0.85(2\pi a^{-1})(1,0,0)$. The vertical energy gap at Γ is 6 ev, but the indirect gap is 2.5 ev. Measurements[15,16] of the ultraviolet absorption show that the indirect transition requires about 5.5 ev. Thus if we were fitting to experiment we would guess the direct gap to be about 9 ev. Since comparatively little is known experimentally about the band structure of diamond, we content ourselves here with a comparison with Herman's model.

The shape of the energy bands obtained from the interpolation scheme is very similar to that sketched by Herman, on the basis of calculations of effective masses at Γ. For comparison Herman's results are shown in Fig. 3, and the results obtained by Slater and Koster by fitting eleven tight-binding parameters to Herman's results are shown in Fig. 4.

From the figures it is clear that the pseudopotential scheme yields results in excellent qualitative agreement with those of Herman, and if Herman's results were more convergent at X and L quite satisfactory quantitative agreement might also be obtained. The tight-binding scheme, on the other hand, yields qualitatively incorrect results. For example, it predicts the conduction band minimum at the center of the zone, and the

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[14] I am grateful to Dr. F. Herman for bringing this point to my attention.

[15] Robertson, Fox, and Martin, Trans. Roy. Soc. (London) A232, 463 (1934).

[16] S. Ramanathon, Proc. Indian Acad. Sci. A24, 137 (1946).

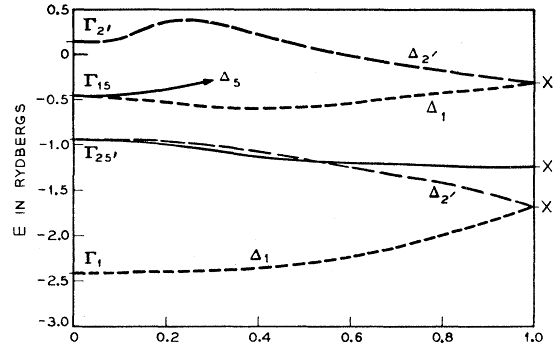

FIG. 3. The energy bands of diamond along the [100] direction, as sketched by Herman[2] on the basis of his orthogonalized plane wave calculations.

valence band maximum elsewhere, whereas the reverse is actually the case. The reason for this can be seen by comparing Fig. 4 with Fig. 1. It is clear that the tight-binding approximation has actually produced an interpolation similar to the one that would be obtained for nearly free electrons. This is because the term values that have been fitted do not lead to a tight-binding picture, but more nearly a free-electron one, so that all overlap integrals approximate those of free electrons. A qualitatively correct shape for the energy bands is obtained from the pseudopotential scheme because it includes enough interaction with higher waves. To include as many states in the tight-binding scheme would probably require the determination of 20 or 30 parameters.

Since the interpolation scheme has yielded the right qualitative shape for the energy bands, it is of some interest to compare quantitatively the effective masses (curvatures) of the energy bands at Γ calculated from the interpolation scheme with those derived by Herman. Without spin-orbit interaction the shape of energy bands near $\Gamma_{25'}$ and Γ_{15} is obtained from the secular equation (see Dresselhaus, Kip, and Kittel[17] and Dresselhaus,[18] whose notation we follow)

$$\begin{vmatrix} Lk_x^2+M(k_y^2+k_z^2)-\lambda & Nk_xk_y & Nk_xk_z \\ Nk_xk_y & Lk_y^2+M(k_x^2+k_z^2)-\lambda & Nk_yk_z \\ Nk_xk_z & Nk_yk_z & Lk_z^2+M(k_x^2+k_y^2)-\lambda \end{vmatrix}=0. \tag{4.4}$$

The values of the constants L, M, and N obtained from the interpolation scheme are compared with those of Herman in Table II. It can be seen the results are in excellent qualitative agreement, but that the interpolation scheme yields constants that are about 30% too large (or effective masses about 30% too small). This is a consequence of truncating the secular equation at a low order. The constants are essentially proportional to a_0b_0, where a_0 and b_0 are the coefficients of the $\langle 111\rangle$ plane waves in expansions of the eigenfunctions belonging to $\Gamma_{25'}^{(1)}$ and $\Gamma_{15}^{(1)}$. Since we are not admitting higher order plane waves, a_0 and b_0 will be somewhat larger than they would be in a more complete expansion. Thus we tend to overestimate the values for the constants.

5. SILICON

We next consider the results for silicon. Calculations were performed for two sets of values of α, V_1, and γ; one set was chosen to fit the orthogonalized plane wave (OPW) calculations of Woodruff[10] and Bassani,[19] while the other set determined V_1 and γ to fit the experimental values of the direct energy gap at $\mathbf{k}=0$ (δE_0)

TABLE II. Values of the constants L, M, and N appearing in Eq. (4.4) of the text, as calculated by Herman[a] and by the interpolation scheme described in the text. The units are rydbergs.

		Herman	Interpolation scheme
$\Gamma_{25'}^{(1)}$	L	−4.07	−4.92
	M	−3.59	−4.93
	N	−5.13	−7.69
$\Gamma_{15}^{(1)}$	L	−2.19	−2.43
	M	2.88	4.40
	N	0.69	1.97

[a] See reference 11.

TABLE III. Comparison of term values for silicon obtained by Woodruff[a] and Bassani[b] in an orthogonalized plane wave calculation with those obtained from the three-parameter interpolation scheme based on experiment which is described in the text. Energies are measured in rydbergs, and the notation for the various representations is that of Herring.[c] Term levels near the energy gap are in boldface. The experimental values discussed in Sec. 7 of the text are also listed.

Term	OPW[a,b]	Interpolation scheme	Exper.
$\Gamma_1^{(1)}$	−1.48	−1.72	
$\Gamma_{25'}^{(1)}$	**−0.86**	**−0.86**	**−0.86**
$\Gamma_{15}^{(1)}$	**−0.54**	**−0.68**	**−0.68**
$\Gamma_{2'}^{(1)}$	**−0.08**	**−0.13**	
$\Gamma_{12'}^{(1)}$		−0.20	
$\Gamma_1^{(2)}$		−0.07	
$X_1^{(1)}$	−1.19	−1.40	
$X_4^{(1)}$	**−0.96**	**−1.10**	
$X_1^{(2)}$	**−0.54**	**−0.75**	**−0.75**
$X_3^{(1)}$	0.09	0.00	
$X_4^{(2)}$	0.24	0.11	
$L_1^{(1)}$		−1.38	
$L_{2'}^{(1)}$		−1.49	
$L_{3'}^{(1)}$		**−0.97**	
$L_3^{(1)}$		**−0.56**	
$L_1^{(2)}$		**−0.58**	**−0.68**

[a] See reference 10.
[b] See reference 19.
[c] See reference 6.

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[17] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).

[18] G. F. Dresselhaus, Ph.D. thesis, University of California, 1955 (unpublished).

[19] F. Bassani, Phys. Rev. **108**, 263 (1957).

and the indirect minimum energy from the top of the valence to the bottom of the conduction band (δE_1). The results were almost the same in both cases, so that we report mainly the values obtained from the second model, which is based directly on experiment. In Table III we list the calculated term values for the second model, for which $\alpha=-1.61$ ry, $V_1=-0.16$ ry, and $\gamma=+0.12$ ry, and compare them with those of the OPW calculations. It can be seen that the two are in excellent agreement, especially when it is remembered that the OPW values are not fully convergent.

The energy bands that are now obtained along the [100] direction are shown in Fig. 5. We find $\delta E_0=0.177$ ry (=2.4 ev) and $\delta E_1=0.11$ ry (=1.5 ev), in approximate agreement with the values observed optically by Dash and Newman.[20] [A slight modification of the parameters could be made to make $\delta E_1=0.08$ ry (=1.1 ev), but this model yields sufficient agreement for our purposes.] In addition, from these curves we can locate the minimum in the conduction band. By solving the secular equation with k_0 [where $\mathbf{k}=k_0 2\pi a^{-1}(1,0,0)$] varying from 0.84 to 0.92 by steps of 0.02, we find the minimum occurs for $k_0=0.88\pm0.02$. The first model, which used $\alpha=-1.54$ ry, $V_1=-0.18$ ry, and $\gamma=+0.12$ ry, yielded $\delta E_0=3$ ev, $\delta E_1=2$ ev, and $k_0=0.86\pm0.02$. These values for k_0 are in excellent agreement with the experimental value of 0.83 ± 0.02 deduced from the fine structure of the recombination radiation observed by Haynes, Lax, and Flood.[21]

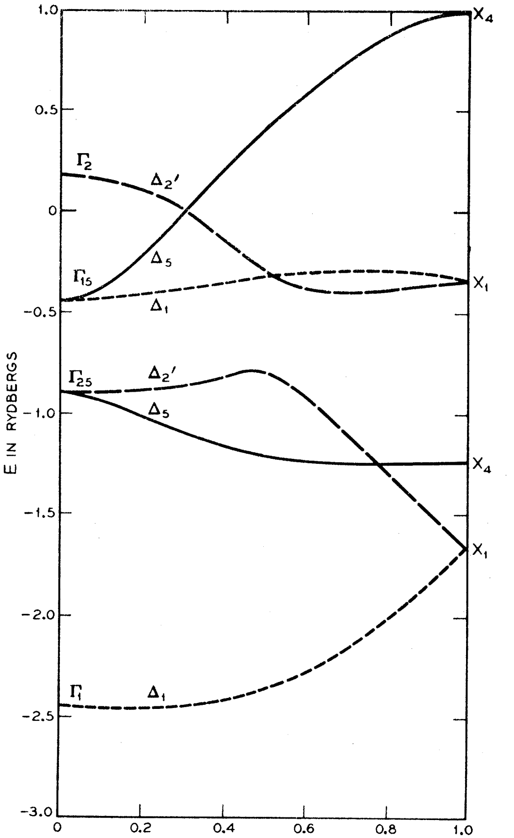

FIG. 4. The energy bands of diamond along the [100] direction, according to the tight-binding interpolation scheme of Slater and Koster.[3]

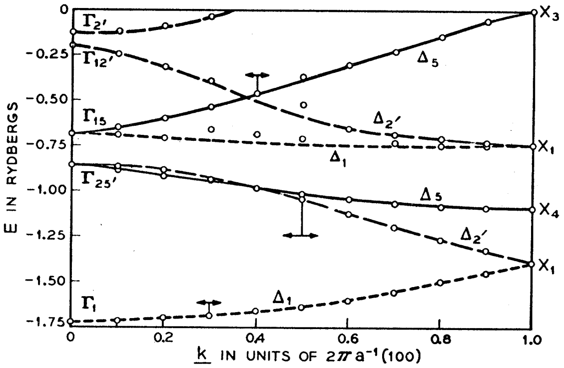

FIG. 5. The energy bands of Si along the [100] direction, as calculated from the interpolation scheme described in the text. The double arrows indicate values of **k** at which discontinuous truncations took place for the various irreducible representations.

The results obtained in Fig. 5 should be compared with those of Bassani,[19] who used the tight-binding interpolation scheme to obtain the bands along Δ. It will be seen that his results for silicon are very similar to those of Slater and Koster for diamond, and are subject to the same criticism.

Once k_0 is known, the effective masses for electrons can be calculated and compared with the values obtained by Dresselhaus, Kip, and Kittle[17] by cyclotron resonance. We find $(m_L^*/m)=0.98$ and $(m_T^*/m)=0.30$, whereas the respective experimental values are 0.98 and 0.19. The agreement for the longitudinal masses is not entirely fortuitous, since it is a consequence of cancellation between small contributions of the lower and next two highest Δ_1 levels that modify the free electron value. On the other hand, the value for the transverse mass is a sensitive function of $E(\Delta_1^{(2)})-E(\Delta_5^{(1)})$ at k_0. If we write this as

$$[E(\Delta_1^{(2)})-E(\Gamma_{25'}^{(1)})]+[E(\Gamma_{25'}^{(1)})-E(\Delta_5^{(1)})]$$

and evaluate the former from experiment and the latter from the OPW values of Table III, we find $(m_T^*/m)\simeq0.18$. However, the OPW values are not convergent, and so are not especially significant. The conclusion is that the theoretical uncertainties in the calculation are too large to warrant including the exchange and

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[20] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

[21] Haynes, Lax, and Flood, Bull. Am. Phys. Soc. Ser. II, **3**, 30 (1958). *Note added in proof.*—B. N. Brockhouse (J. Phys. Chem. Solids, to be published) has recently pointed out that the interpretation given by Haynes, Lax, and Flood of their data is not consistent with the vibration spectrum of Si as deduced from other experiments. The value of k_0 has also been deduced by G. Feher (J. Phys. Chem. Solids, to be published) from resonance studies of donor-electron wave functions. He finds $k_0=0.85$, in good agreement with our results.

TABLE IV. Constants appropriate to the top of the valence band in silicon. The constants, which are described in the text, are measured in units of $\hbar^2/2m$, and the results obtained by various workers from experiment and theory are compared.

	A	$\|B\|$	$\|C\|$	L	M	N	H_1	F	G
DKK[a] (exper.)	−4.1	1.6	3.3						
DZL[b] (exper.)	−4.0	1.1	4.0						
DKK[a] (theory)	−4.1	1.6	3.3	−1.9	−6.7	−7.5	−6.7	−1.2	−0.4
D[c] (theory)	−4.0	1.1	4.0	−7.2	−3.9	−7.7	−3.9	−4.9	−1.1
Pseudopotential	−3.9	0.9	3.6	−3.1	−5.8	−6.7	−5.8	−1.7	−0.7
Compromise	−3.9	1.1	3.6	−2.7	−6.0	−7.0	−6.0	−1.5	−0.6

[a] See reference 17.
[b] Dexter, Zeiger, and Lax, Phys. Rev. **104**, 637 (1956).
[c] See reference 18.

truncation corrections mentioned at the end of this section.

We now consider the bands near the top of the valence band at $\Gamma_{25'}$. In order to compare our results with those obtained from cyclotron resonance, it is necessary to include the effects of spin-orbit coupling. When this is done, the energy surfaces of interest have the form[17,18]

$$E \cong Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2+k_y^2k_z^2+k_x^2k_z^2)]^{\frac{1}{2}}, \quad (5.1)$$

where

$$A = \hbar^2/(2m) + (L+2M)/3,$$
$$B^2 = [(L-M)/3]^2, \quad (5.2)$$
$$C^2 = \tfrac{1}{3}[N^2 - (L-M)^2].$$

Here A, B, C, L, M, and N are measured in units of $\hbar^2/2m$. Dresselhaus[18] has shown that the constants L, M, and N, which previously appeared in Eq. (4.4), have the form $L = F+2G$, $M = H_1+H_2$, and $N = F-G+H_1-H_2$. Here, for $\Gamma_{25'}$,

$$F = \frac{\hbar^2}{m^2} \sum_{\Gamma_{2'}^{(i)}} \frac{|(\Gamma_{25'}^{(1)}|p_x|\Gamma_{2'}^{(i)})|^2}{E_1-E_i}, \quad (5.3)$$

$$G = \frac{\hbar^2}{m^2} \sum_{\Gamma_{12'}^{(i)}} \frac{|(\Gamma_{25'}^{(1)}|p_x|\Gamma_{12'}^{(i)})|^2}{E_1-E_i}, \quad (5.4)$$

$$H_1 = \frac{\hbar^2}{m^2} \sum_{\Gamma_{15}^{(i)}} \frac{|(\Gamma_{25'}^{(1)}|p_y|\Gamma_{15}^{(i)})|^2}{E_1-E_i}, \quad (5.5)$$

$$H_2 = \frac{\hbar^2}{m^2} \sum_{\Gamma_{25}^{(i)}} \frac{|(\Gamma_{25'}^{(1)}|p_y|\Gamma_{25}^{(i)})|^2}{E_1-E_i}. \quad (5.6)$$

In the matrix elements occurring in Eqs. (5.3)–(5.6), for example, $\Gamma_{2'}^{(i)}$ denotes an appropriate basis function. as defined by Dresselhaus.[18] From the experimental values[17] (in units of $\hbar^2/2m$), $A = -4.1 \pm 0.2$, $|B| = 1.6 \pm 0.2$, and $|C| = 3.3 \pm 0.5$, two sets of values for L, M, and N have been deduced.[12,13] It was originally hoped that results from the interpolation scheme could differentiate between these two. However, this has proved unnecessary, since the second model is based on an arithmetic error. In deducing F, G, and H_1 from L, M, and N, one assumes $H_2 \simeq 0$ due to the remoteness of the nearest Γ_{25} level. Then from $L = -7.2$, $M = 3.9$, $N = -7.7$, one finds the correct values $H_1 = -3.9$, $F = -4.9$ and $G = -1.1$. However, it is easy to see that H_1 (the term due to $\Gamma_{15}^{(1)}$) must have a magnitude about 3 times that of F (which is due to $\Gamma_{2'}^{(1)}$). Thus this model must be incorrect.[22–24]

The values of the various constants have been calculated by using the term values derived from the pseudopotential. These are listed in Table IV, together with the experimental results of Dresselhaus, Kip, and Kittel[17] and Dexter and Lax.[25] The various models are also listed, and in the last line a model is proposed which, in the author's opinion, represents a good compromise between the experimental and theoretical results. (This model is rather similar to the one first proposed by Dresselhaus, Kip, and Kittel.[17]) A comment that is appropriate here is that A, B, and C, as calculated from the interpolation scheme, are in rather too good agreement with the experimental values. From the comments made at the end of Sec. 4, we would have expected the interpolation scheme to overestimate these constants somewhat. Actually the good agreement is a result of a fortuitous cancellation of two errors. This will be discussed further at the end of the next section.

It is perhaps worth emphasizing here that the model that we have constructed for silicon determines its two parameters from experiment (δE_0 and δE_1) and then predicts six other values [k_0, (m_L^*/m), (m_T^*/m), A, $|B|$, $|C|$] which are in good agreement with the results of various measurements.

6. GERMANIUM

Since the term scheme for Ge, even at the center of the zone, is considerably different from that of diamond and Si, it is interesting to consider the results obtainable from the pseudopotential scheme when it is applied to Ge. Before we present these results we review briefly what is known about the levels near the energy gap.

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[22] Since this model has been used in several calculations, (see references 24 and 25) it is significant that band theory shows that it is incorrect.

[23] W. Kohn in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 5.

[24] E. O. Kane, J. Phys. Chem. Solids **1**, 82 (1956).

[25] R. N. Dexter and B. Lax, Phys. Rev. **96**, 223 (1954).

The most important difference between the energy bands of Si and Ge is that in Si the antibonding p state, Γ_{15}, lies lower than the antibonding s state, $\Gamma_{2'}$, whereas the opposite case obtains for Ge, as was first shown by Herman.[2,26] In a sense this means the bands of Ge are nearer those that would be obtained in the tight-binding approximation. Thus in Ge an extra parameter is necessary to fit the term levels even approximately, and this we take to be $\beta = V_{220}$, so that our prescription for the Fourier coefficients of the pseudopotential is now

$$V_{000}=\alpha, \quad V_{<111>}=V_1\cos[8^{-1}(K_1+K_2+K_3)a],$$
$$V_{<220>}=\beta\cos[8^{-1}(K_1+K_2+K_3)a],$$
$$V_{\mathbf{K}}=\gamma\cos[8^{-1}(K_1+K_2+K_3)a],$$
$$\mathbf{K}\neq 0,\ \langle 111\rangle,\ \langle 220\rangle. \tag{6.1}$$

In Ge we find a good fit is obtained by taking $\alpha=-0.60$ ry, $V_1=-0.25$ ry, $\beta=0.011$ ry, $\gamma=0.05$ ry. By comparing these values with those used for Si we can understand the significance of the parameters. The parameter V_1 is negative in both cases, and represents the bonding effect due to the valence electrons. Both β and γ are considerably smaller in Ge than in Si; β is used to adjust the relative levels of $\Gamma_{2'}$ and Γ_{15}. It is clear that the result $\beta=\gamma$, which occurred in Si, is in general a fortuitous one. Finally, in Ge we have fitted our four parameters to the five term values $\Gamma_{25'}{}^{(1)}$, $\Gamma_{2'}{}^{(1)}$, $\Gamma_{15}{}^{(1)}$, $L_1{}^{(2)}$, and $X_1{}^{(2)}$. The second of these is obtained from Dash and Newman's results[20]; the fourth is determined from the indirect energy gap, and the last can be obtained by extrapolating measurements of the energy gap in Ge-Si alloys.[27,28] $\Gamma_{15}{}^{(1)}-\Gamma_{25'}{}^{(1)}$ can be determined reasonably well from Herman's calculations, since the difference is relatively insensitive to the stage of convergence.

The results that are obtained with this choice of parameters are listed in Table V, which also shows Herman's values and the values obtained from experiment. (The zeros of energy have been chosen so that all three columns have approximately the same value for $\Gamma_{25'}{}^{(1)}$.) From the table it is seen that the results agree with the experimental values to within 0.05 ry, and with Herman's value of $\Gamma_{15}{}^{(1)}$ to within 0.1 ry, which is about the probable error of Herman's calculations.

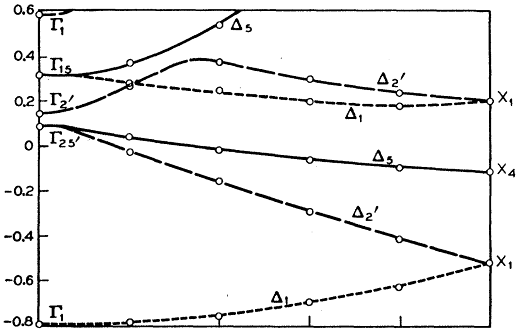

FIG. 6. The energy bands of Ge along the [100] direction, as calculated from the interpolation scheme described in the text.

TABLE V. Comparison of term values for germanium obtained by the interpolation scheme described in the text with those obtained by Herman[a] in an orthogonalized plane wave calculation, and with values deduced from experiment. Energies are measured in rydbergs, and the notation for the various representations is that of Herring.[b] Term levels near the energy gap are in boldface.

Term	Herman	Interpolation scheme	Exper.
$\Gamma_1{}^{(1)}$	−0.76	−0.80	
$\Gamma_{25'}{}^{(1)}$	**0.09**	**0.09**	**0.09**
$\Gamma_{2'}{}^{(1)}$	**0.20**	**0.15**	**0.15**
$\Gamma_{15}{}^{(1)}$	**0.42**	**0.32**	
$\Gamma_1{}^{(2)}$		0.59	
$X_1{}^{(1)}$	**−0.50**	**−0.52**	
$X_4{}^{(1)}$	**−0.04**	**−0.10**	
$X_1{}^{(1)}$	**0.44**	**0.20**	**0.17**
$L_1{}^{(1)}$	−0.37	−0.39	
$L_{2'}{}^{(1)}$	−0.65	−0.62	
$L_{3'}{}^{(1)}$	**−0.01**	**0.06**	
$L_1{}^{(2)}$	**0.34**	**0.19**	**0.14**
$L_3{}^{(1)}$	0.56	0.56	

[a] See reference 21.
[b] See reference 6.

The values obtained for the constants characterizing the top of the valence band at Γ are (in units of $\hbar^2/2m$): $L=-18.7$, $M=-3.6$, $N=-20.7$, $A=-7.6$, $|B|=5.0$ and $|C|=8.4$. The experimental values are $A=-13.0$, $|B|=8.9$, $|C|=10.3$. In the case of Ge we have not obtained such good agreement with the results of experiment as we did for Si. This is because our calculations of effective masses are limited not only by truncation errors, as was discussed in connection with diamond, but also by exchange corrections due to the nonlocal character of the exchange potential. In the case of Si there is a fortuitous cancellation of the two effects, but in Ge, where the chief perturbation is due to the $\Gamma_{2'}$ level instead of the Γ_{15} level, this does not occur. The exchange corrections are discussed in detail elsewhere.[29]

Energy bands along Δ have been calculated using this pseudopotential; the results are shown in Fig. 6. They are similar to the results obtained by Herman.[26] In addition the effective masses for electrons in the conduction band at L have been calculated. One obtains $(m_L{}^*/m)=1.27$, compared with the experimental value of 1.58. For the transverse mass we find $(m_T{}^*/m)=0.15$, whereas the experimental value is 0.082. Agreement with experiment is improved if the experimental value of $L_1{}^{(2)}$ is introduced. Thus if one computes $E(L_1{}^{(2)})-E(L_{3'}{}^{(1)})$ from $[E(L_1{}^{(2)})-E(\Gamma_{25'}{}^{(1)})]-[E(\Gamma_{25'}{}^{(1)})-E(L_{3'}{}^{(1)})]$ and uses for the

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[26] F. Herman, Physica **20**, 801 (1954).
[27] E. R. Johnson and S. M. Christian, Phys. Rev. **95**, 560 (1954).
[28] Braunstein, Moore, and Herman, Phys. Rev. **109**, 695 (1958).
[29] J. C. Phillips, J. Phys. Chem. Solids **7**, 52 (1958).

former term the experimental value of 0.045 ry and for the latter the value 0.03 ry obtained from the pseudopotential values listed in Table V, one finds $(m_T^*/m)=0.09$, in very good agreement with experiment. Since truncation and nonlocal effects have not been included in the calculation, the agreement is partially fortuitous. It is believed that it is not entirely so, however, since it would appear that in this case the truncation and nonlocal corrections tend to cancel, as they did for the holes in Si. Incidentally, this argument suggests that the pseudopotential value for $L_{3'}^{(1)}$ is quite satisfactory.

The results that have been presented show that the model that has been constructed for Ge is as successful as that constructed for Si in fitting a large number of experimental facts with a model depending on only a few disposable parameters. As was pointed out in the beginning of this section, the energy bands of Ge and Si are qualitatively rather different, so that it is reassuring that the method is successful in both cases.

7. ENERGY BANDS OF Si AND Ge AS DEDUCED FROM EXPERIMENT

We are now in a position to take advantage of the "bridge" that we have constructed and so sketch the highest valence and lowest conduction bands of Si and Ge in the [100] and [111] directions with some accuracy, using wherever possible the experimental facts. These are as follows:

(1) the direct energy gap, as determined optically by Dash and Newman[20];

(2) the locations of the minima in the conduction bands, and the indirect energy gaps, thus yielding $E(X_1^{(2)})$ and $E(L_1^{(2)})$ for Si and Ge, respectively;

(3) the converse values, as determined from extrapolating measurements[27,28] on Ge-Si alloys [although $E(L_1^{(2)})$ for Si is somewhat unreliable, on a ry scale the uncertainty is still small];

(4) the location of the minimum in the (100) direction in Si, as determined from the fine-structure of recombination radiation[21]; and

(5) the direct valence-conduction band gaps at X and L for Si and Ge, respectively, as can be inferred from the transverse effective masses for electrons.

These experimental facts lead to only slight modifications of the term values already calculated. The effective masses (curvatures) may then be modified by assuming that the matrix elements are unchanged but taking into account the change in the energy gaps. (This is a good approximation since ordinarily most of the curvature at symmetry points is produced by interactions between different irreducible representations.) Finally, the remaining interpolation curves are sketched by comparison with the results of Secs. 5 and 6, which should be approximately correct here also because of the approximate agreement of the interpolation term values with the experimental ones. The results are shown in Figs. 7 and 8. The curves so obtained should be accurate to about 0.05 ry at worst. Probable errors in various term values at symmetry points are indicated in the figures by brackets.

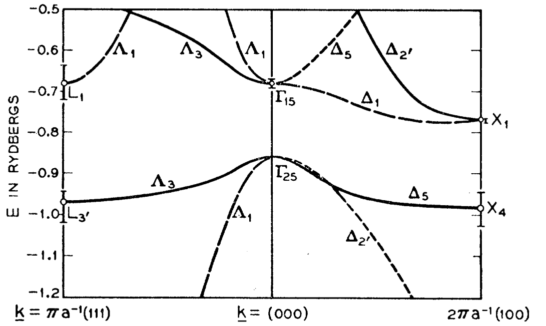

FIG. 7. The energy bands of Si near the energy gap. The figure summarizes all that is deduced about the shape of the bands by combining experimental and theoretical information in the way described in Sec. 7. Probable errors for term values at the center and edge of the Brillouin zone are also indicated.

It is clear that if the use of a simple interpolation scheme has led to the bands along the [100] and [111] directions, then a more elaborate scheme, using perhaps 5 or 6 parameters and larger determinants to obtain a fit to the results of Figs. 7 and 8, can be used to extend the latter results to other directions in the Brillouin zone. This approach would yield the bands near the energy gap for all **k**. On the other hand, if all that is desired is the density of states near the valence and conduction band edges, this quantity can be obtained much more simply by applying the moment-singularity method developed by Lax and Lebowitz[30] and the author[31] to the present models. All that is required in this approach are term values and curvatures for critical points of the band surfaces near the energy gap. Most of these quantities can be deduced from experiment, using effective masses and term values deduced from Figs. 7 and 8. Critical points not located at symmetry points can be discovered by group-theoretical and topological arguments[31] and their term values and curvatures estimated from the interpolation models developed in Secs. 5 and 6. It should be noticed that in practice most of the additional critical points will still lie on symmetry lines of the zone. This is an important point, since it greatly reduces the order of the secular equations to be solved, and greatly simplifies the perturbation theory necessary to calculate the transverse curvatures. In this way one can circumvent the very considerable amount of labor that would be required to sample solutions of the secular equation at general points of the zone, since even our truncated interpolation scheme leads to secular equations of order 25 at such points.

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[30] M. Lax and J. L. Lebowitz, Phys. Rev. **96**, 594 (1954).

[31] J. C. Phillips, Phys. Rev. **104**, 1263 (1956).

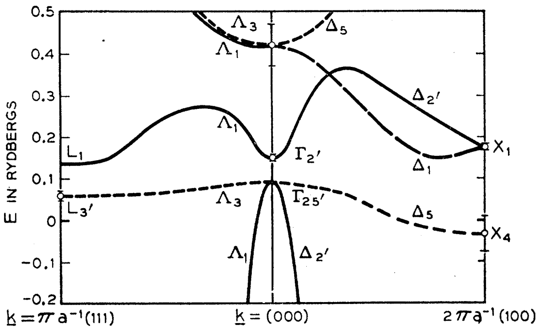

FIG. 8. The energy bands of Ge near the energy gap. The figure summarizes all that is deduced about the shape of the bands by combining experimental and theoretical information in the way described in Sec. 7. Probable errors for term values at the center and edge of the Brillouin zone are also indicated.

Finally, we remark that in the bands sketched in Figs. 7 and 8 the effects of spin-orbit coupling are neglected; these are probably important only at the top of the valence band at Γ, and the behavior of the bands in the neighborhood of Γ has been discussed by several authors.[18,24]

8. CONCLUSIONS

The results obtained from an interpolation scheme should not be taken too seriously. Nevertheless the great success, both qualitative and quantitative, that we have had in correlating many experimental values related to the energy band structures of Ge and Si by schemes based on a few parameters justifies several comments.

First, we have obtained satisfactory shapes for the bands only by including interaction with a sufficiently large number of the higher conduction band states. This is because the shape of the bands away from the symmetry points of the Brillouin zone is determined primarily by kinetic energy terms and second-order perturbations from other levels.

We also see that the simple scheme that has been discussed here provides a convenient bridge between experimental results and extensive and laborious band calculations. This device was used to good effect to sketch the energy bands of Ge and Si in Sec. 7. Moreover, the general similarity between the various schemes for silicon suggests that although Woodruff[10] did not concentrate his attention on obtaining a realistic crystal potential, it may well be that if his calculations were carried through to a convergent conclusion they would yield results more nearly in agreement with experiment than those that have been obtained for any other complicated band structure. In addition, it is easy to see how slight modifications of the crystal potential could remove the remaining discrepancies.

In this connection the present work suggests the possibility of using the OPW method to construct a crystal potential that would yield energy bands in agreement with experiment. Previously Herman[26] suggested that something like this might be done by adjusting the values of the core levels E_{nl} (this might be especially appropriate for the $3d$ levels in Ge, with which Herman was especially concerned). Our viewpoint is somewhat different. We suggest that the first few Fourier coefficients of the potential be allowed to vary somewhat. In any calculation of the potential from first principles these are the quantities that are most uncertain, while the higher coefficients, which are associated with the core, may be determined from self-consistent calculations for the atom. By proceeding in this way one includes the effect of the shape of the unit cell and bonding in an empirical way.

Finally, we remark that if a method based on plane waves is successful for semiconductors, a similar treatment should certainly be valid for metals. Again one could hope to determine the parameters either from theory or experiment. Something like this has been done by Heine[32] for aluminum. For metals, however, the matter is more difficult, since one is concerned with "pockets" of the Fermi surface near zone boundaries, and the principal curvatures of pockets are not so basic to the band structure as are effective masses *and* energy gaps.

ACKNOWLEDGMENTS

The author is grateful to Dr. C. Herring for suggesting this problem, and for several conversations. The work was greatly simplified by using factored secular determinants and symmetrized combinations of plane waves which were generously supplied by Dr. F. Herman, to whom the author is grateful also for several conversations. The program for solving the determinants was supplied by Dr. D. Kleinman, and the calculations were programed by Mrs. W. Mammel and Mrs. L. Lee, whom the author thanks for their generous assistance.

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[32] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).