

## General model pseudopotential: Binary compounds

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A simple general-model pseudopotential is introduced, which is particularly suitable for energy-band calculations in binary and more-complex semiconductors. It includes a point-charge Coulomb potential plus a repulsive core part whose simple analytical form in both direct and reciprocal space is characterized by three independent parameters. The resulting ionic potentials are screened by a semiconducting dielectric function; off-diagonal screening effects are accounted for in heteropolar compounds by explicitly adding to the Hamiltonian the contribution due to the charge transfer. The electronic band structure of the III-V and II-VI compounds has been accordingly computed and a good agreement has been obtained with previously published results. The ionicities computed from the corresponding charge transfers turn out to be rather close to the Phillips values.

### I. INTRODUCTION

A few years ago it was claimed<sup>1</sup> through the aid of a remarkably large quantity of numerical data that it should be possible to produce, within a common theoretical framework, useful pseudopotentials for many elements in many situations. Though no general theorem justifies the use of superposition and linearity principles for the pseudopotentials, this claim seems to apply to semiconducting compounds as well as to normal metals. Actually some satisfying semiconductor band structures have been calculated<sup>2,3</sup> by using the Heine-Abarenkov<sup>4</sup> model potential screened by a Penn-type<sup>5</sup> dielectric function. This method, however, did not prove to have a wider applicability.

In this paper we suggest that a substantial improvement over the above approach can be gained by replacing the Heine-Abarenkov model potential with a new one whose built-in features make it look much more promising for solid-state calculations. It turns out that a local, energy-independent, general-model pseudopotential can be found so to obtain satisfying band structures for the groups IV, III-V, and II-VI semiconductors. The positive outcome of such a fitting program is in itself a notable result: a more important point, however, is that this end has been accomplished without sacrificing (or, maybe better, thanks to) the physical meaning of the parameters introduced. In this connection a particularly interesting feature is the introduction in the Hamiltonian of the contribution due to the charge transfer which occurs in heteropolar compounds.

As is reported elsewhere<sup>6</sup> our approach proved

to be easily applicable to band-structure calculations of ternary compounds without any readjustment of the parameters. In Sec. II we define our general-model pseudopotential and discuss the physical meaning of its parameters. The resulting curves in real and reciprocal space for all of the elements we have considered are given in Sec. III together with the band structures we have computed. Section IV contains a summary and some concluding remarks.

### II. GENERAL-MODEL PSEUDOPOTENTIAL

A model potential may be defined as a physically meaningful expression whose parameters are to be determined by some fitting procedure. Heine and Abarenkov<sup>4</sup> fitted the parameters of their model to the atomic energy levels, therefore being able to make an independent evaluation of each one of their potentials. If the fitting is made to the optical spectra of heteropolar compounds such independent evaluations are no longer feasible and the whole process of finding some "best" set of parameters may become very involved. In retribution, however, one may get far more accurate band structures than in the preceding case; furthermore in this way the transferability of pseudopotentials<sup>1</sup> may be given a quite unambiguous formal definition.

According to the above discussion our basic idea was to look for a model potential capable to describe satisfyingly the known band structures of binary semiconductors. The extension to more complex compounds is then quite straightforward and is obviously an important test of the physical reliability of the resulting potentials.

We chose to look for a local and energy-inde-

pendent potential which has a simple analytical expression in both direct and reciprocal space. Neglecting nonlocality and energy-dependence effects stemmed out from our feeling that such an approximation would have been consistent with the limited overall accuracy attainable in band structures computed with a small number of parameters for a great number of compounds. The requirement of simple analytical forms was dictated both by simplicity and physical reasons; in fact the use of an analytical expression for the model potential in reciprocal space considerably eased the fitting process, whereas the analogous choice in real space allowed a more direct physical interpretation of the parameters.

We started from the following expression for the bare potential in real space

$$V(r) = \alpha e^{-\beta r^2} \sin \gamma r / r - Ze^2 / r, \quad (1)$$

where  $Z$  is the number of the valence electrons of the element under consideration and  $\alpha$ ,  $\beta$ , and  $\gamma$  are disposable constants. This potential has no discontinuities in the relevant range of  $r$  values and is made up by a Coulombic part plus a repulsive core term, thus reflecting two essential features of the true potential. The particular form chosen for the core term has the important property of being easily Fourier transformed. In reciprocal space we get

$$V(q) = A e^{-Bq^2} \sinh(Cq) / q - 4\pi Ze^2 / q^2, \quad (2)$$

where  $A$ ,  $B$ ,  $C$  are connected to the preceding constants  $\alpha$ ,  $\beta$ , and  $\gamma$  through the relations

$$A = \frac{1}{2} [\alpha (\pi / \beta)^{1/2} e^{-\gamma^2 / 4\beta}], \quad (3)$$

$$B = 1/4\beta, \quad (4)$$

$$C = \gamma/2\beta. \quad (5)$$

The fitting process developed as follows: First of all, systematic energy-band calculations based on plane-wave expansions were performed for the elemental semiconductors Si, Ge, and Sn by regularly varying the values of the parameters. The "best" values of  $\alpha$ ,  $\beta$ , and  $\gamma$  were then used as starting values for the elements of the corresponding rows of the Periodic Table. It must be noted that in all our calculations the bare potential has been screened by the Schulze and Unger<sup>7</sup> dielectric function corrected for exchange through the Hubbard<sup>8</sup> approximation. As is shown in Table II the resulting band structures of Si, Ge, and Sn compare quite satisfyingly with those ones of Cohen and Bergstresser.<sup>9</sup>

The next step was to seek the laws of variation of our parameters along each row. An important clue was gained by connecting the height and the width of the core part in real space with the cor-

responding features of the actual atomic cores. The real breakthrough, however, was to regard  $Z$  too as an adjustable parameter in heteropolar compounds, subject to the condition that the sum of the valence charges over the unit cell should remain unchanged. The point, as is stated more precisely in Sec. III, is that in this way one essentially introduces in the Hamiltonian the contribution due to the charge transfers that characterize the ionic bond. Therefore this choice allows the core-part parameters to be fitted to essentially atomic features, without being influenced by the particular strength of the ionic bond involved in the formation of the compound. Of course the charge transfers are supposed to be of the point-charge type and localized at the atomic sites. This approximation notwithstanding we feel that this specific attention to the problem of the ionic bond is the key, together with the use of a proper dielectric function, of the success of our fitting program.

As it was to be expected from the preceding discussion the values of  $\alpha$ ,  $\beta$ , and  $\gamma$  turned out to be relatively slowly varying for elements on the same row of the Periodic Table. The best results were obtained by keeping  $\beta$  constant along each row and varying  $\alpha$  and  $\gamma$  in a nearly symmetrical way around its value for the group-IV element. The regularity of the variations of  $\alpha$  and  $\gamma$  along the rows is shown in Fig. 1, where the corresponding values are plotted versus the atomic number.

### III. NUMERICAL RESULTS

Our resulting model potentials in real and reciprocal space are reported in Figs. 2-7. The corresponding parameters are listed in Table I together with some of the main features of the

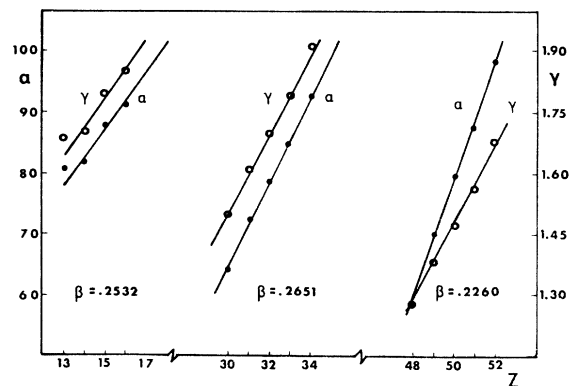


FIG. 1. Repulsive part parameters as a function of the atomic number.

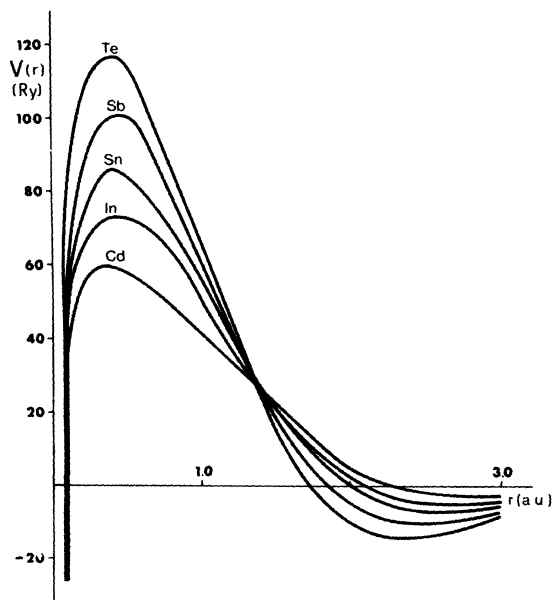


FIG. 2. Bare atomic potentials of the elements of the Sn row.

curves. It may be observed that in spite of their being fitted to the optical spectra of heteropolar compounds, our potentials look as if they could be easily derived just from some set of known atomic parameters. It is particularly interesting to note the close linear relationships that con-

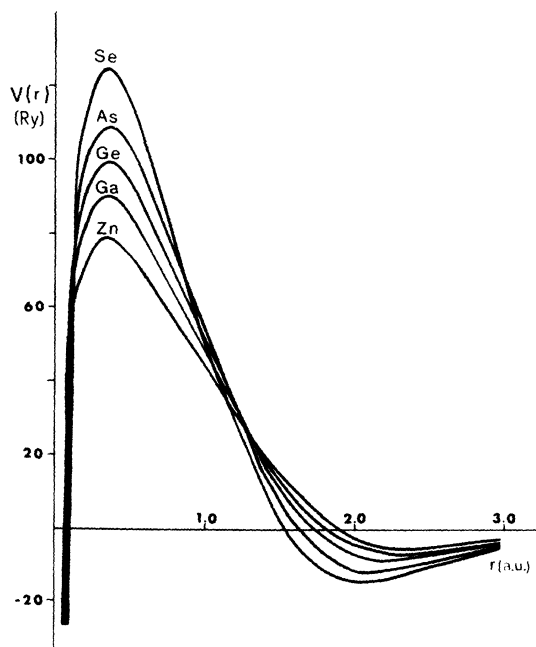


FIG. 3. Bare atomic potentials of the elements of the Ge row.

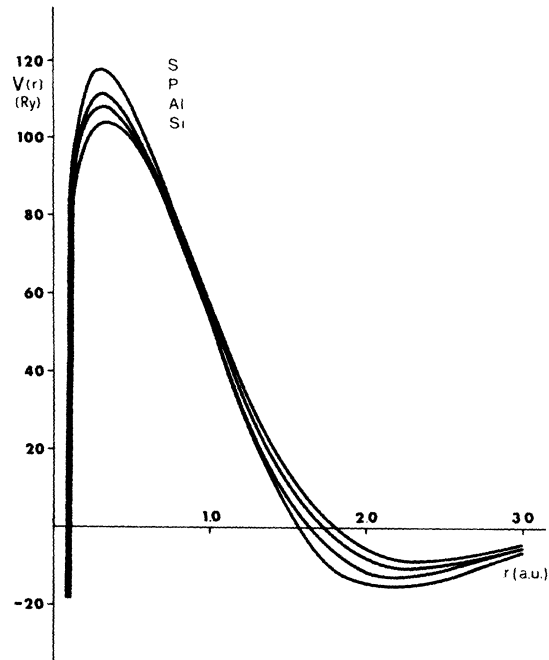


FIG. 4. Bare atomic potentials of the elements of the Si row. The inversion with respect to the usual order P-Si-Al is limited to the core region.

nects (Fig. 8) our  $r_0$  values [i.e., the values of  $r$  for which  $V(r)=0$ ] to a set of tabulated values of ionic radii. In Fig. 8 the different slope corresponding to the elements of the Si row in our opinion reflects the absence of the  $d$  orbitals in their cores.

The complete set of interband transitions which have been considered in our fitting program is listed in Table II where a comparison is made among our values, the experimental data and the Cohen and Bergstresser's<sup>9</sup> completely empirical

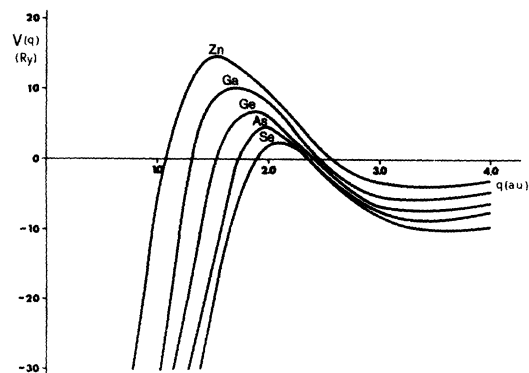


FIG. 5. Bare atomic potentials in reciprocal space for the Ge row.

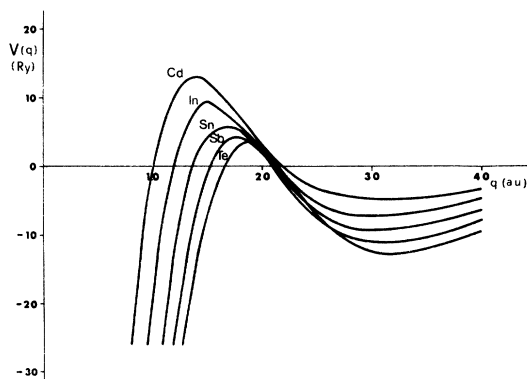


FIG. 6. Bare atomic potentials in reciprocal space for the Sn row.

previous fitting. Some of our corresponding band structures are reported in Figs. 9–11. No significant inconsistency appears to exist among the three sets of data reported in Table II and our fitting may thus be considered as successful. In other words we might say that the Cohen and Heine<sup>1</sup> claim which has been referred to in the Introduction has now been substantiated.

Some special attention should be given to the implication of our regarding the valence charges  $Z$  as adjustable parameters. Let us write our one-electron Hamiltonian as follows:

$$H = H_0 + V_B(r) + V_H(r) + V_T(r), \quad (6)$$

where  $H_0$  is the kinetic energy term,  $V_B$  our bare pseudopotential,  $V_H$  the Hartree self-consistent field, and  $V_T$  the contribution due to the charge transfers, i.e., to a nonlinear response of the electron density to the ionic potential. For a binary compound  $AB$   $V_B$  may be written as

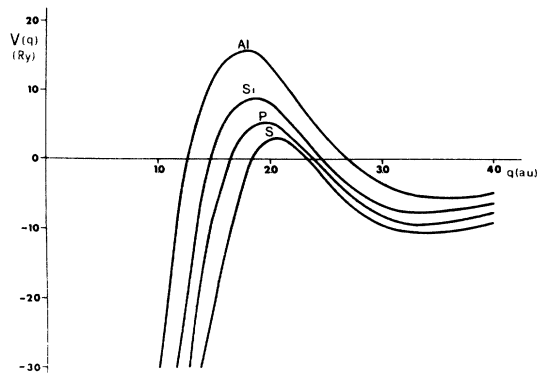


FIG. 7. Bare atomic potentials in reciprocal space for the Si row.

TABLE I. Atomic parameters for our model potential together with the values of  $r_0$  [ $V(r_0) = 0$ ] and  $q_0$  [ $V(q_0) = 0$ ] in a.u.

	$\alpha$	$\beta$	$\gamma$	$r_0$	$q_0$
Al	81.00	0.2532	1.692	1.76	1.25
Si	82.06	0.2532	1.708	1.71	1.50
P	87.84	0.2532	1.796	1.63	1.65
S	91.52	0.2532	1.853	1.52	1.90
Zn	64.67	0.2651	1.502	1.95	1.10
Ga	72.60	0.2651	1.611	1.82	1.30
Ge	78.86	0.2651	1.700	1.71	1.55
As	85.06	0.2651	1.791	1.62	1.70
Se	92.70	0.2651	1.906	1.51	1.90
Cd	58.94	0.2260	1.286	2.29	1.00
In	70.13	0.2260	1.382	2.09	1.20
Sn	79.48	0.2260	1.473	1.96	1.40
Sb	88.51	0.2260	1.567	1.84	1.55
Te	98.45	0.2260	1.678	1.72	1.65

$$V_B(r) = \sum_{\vec{I}_A, \vec{I}_B} \left( -\frac{Z_A e^2}{|\vec{r} - \vec{I}_A|} - \frac{Z_B e^2}{|\vec{r} - \vec{I}_B|} + U_A^R(\vec{r} - \vec{I}_A) + U_B^R(\vec{r} - \vec{I}_B) \right), \quad (7)$$

where  $\vec{I}_A$  and  $\vec{I}_B$  denote the lattice points for the ions  $A$  and  $B$  and  $U_A^R$  and  $U_B^R$  are repulsive core terms as in Eq. (1). As usual in pseudopotential calculations  $V_H$  is accounted for by introducing a suitable dielectric function, in our case the one by Schulze and Unger.<sup>7</sup> The charge transfer  $V_T$

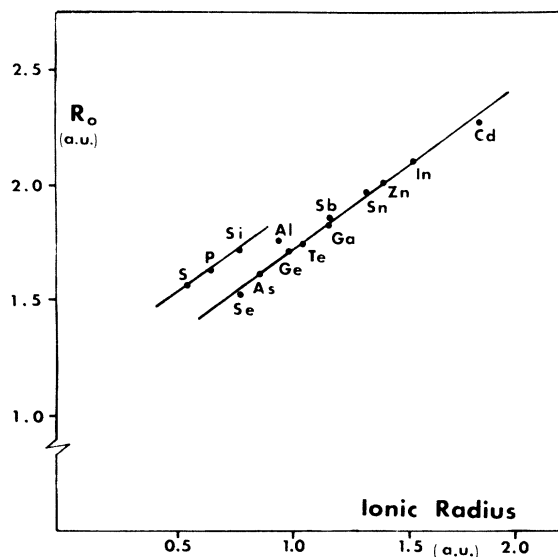


FIG. 8.  $R_0$  values [ $V(R_0) = 0$ ] versus ionic radii as tabulated in *Handbook of Chemistry and Physics*, 49th ed., edited by R. C. Weast (Chemical Rubber, Cleveland, Ohio, 1968), p. F152.

TABLE II. Main interband transitions energies in eV, with symmetry labels appropriate to the diamond structure. Columns 1 give the experimental values, columns 2 our values, while columns 3 refer to values of Ref. 9. Unmarked values of columns 1 are quoted from Ref. 9.

	$\Gamma_2 - \Gamma_{25}^*$			$\Gamma_{15} - \Gamma_{25}^*$			$L_1 - \Gamma_{25}^*$			$X_1 - \Gamma_{25}^*$			$L_1 - L_3$			$X_1 - X_4$			$\Delta Z$
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	
Si		3.4	3.8	3.4	3.4	3.4	1.8	1.9		1.1	1.2	0.8	3.2	3.0	3.1	4.1	4.2	4.0	0.0
AlP	3.6 <sup>a</sup>	3.6			5.2		3.4			2.5 <sup>a</sup>	2.6		4.2			4.9			0.25
AlAs	3.1 <sup>a</sup>	2.8		4.4	4.4		2.3 <sup>a</sup>	2.4		2.2 <sup>a</sup>	2.3		4.0 <sup>a</sup>	3.3		4.6 <sup>a</sup>	4.6		0.65
GaP	2.8	2.9	2.7	4.9	5.0	5.3	2.6	2.7		2.3	2.3	2.2	3.6	3.5	3.6	5.1	4.7	4.6	0.35
ZnS	3.8	3.5	3.7	7.1	7.3	8.9	4.2	5.3		3.8	5.2		5.9	4.9	5.8	6.8	5.7	6.7	0.90
AlSb	2.1	2.1	1.9	3.9	3.5	4.1	1.9	1.9	2.0	1.9	2.2	2.0	2.9	2.6	2.8	4.2	4.1	3.9	0.70
GaAs	1.4	1.5	1.4	4.6	4.7	4.5	1.9	1.7		1.9	2.3	1.8	2.5	2.7	2.6	4.6	4.5	4.0	0.50
InP	1.4	1.4	1.6	4.8	4.9	4.6	1.5	2.0		1.8	2.3		3.1	2.2	2.8	4.4	3.6	4.2	0.80
Ge	1.0	0.9	1.2	3.4	3.5	3.5	0.8	0.9	0.9	1.0	1.4	1.0	2.1	2.0	2.0	4.3	4.0	3.8	0.0
ZnSe	2.9	2.9	2.9	6.8	7.9		3.5	4.5		3.9	4.5		5.0	4.0	5.0	6.4	5.4	6.0	1.25
GaSb	1.0	0.8	0.8	4.0	3.8	4.4	1.1	1.4	1.6	1.1	2.1	2.1	1.8	2.2	2.3	4.1	3.9	3.8	0.20
InAs	0.5	0.4	0.5	4.5	4.9	4.6	1.3	1.6		2.0	2.1		2.3	1.9	2.3	4.5	3.6	3.9	0.75
ZnTe	2.6	2.7	2.5	5.1	5.2	6.7	2.8	3.8		3.0	4.0		3.8	3.3	4.3	5.3	4.5	5.2	1.10
Sn	-0.2	-0.1	-0.1	2.9	2.9	3.0	0.3	0.5	0.6	1.3	1.1		1.4	1.3	1.4	3.5	3.2	3.1	0.0
InSb	0.5	0.5	0.6	3.7	3.8	4.1	1.2	1.5		1.8	2.0		2.0	1.8	2.1	4.0	3.3	3.5	0.55
CdTe	1.9	1.9	2.0	6.3	6.0	6.6	2.6	3.5		3.0	4.0		3.5	3.0	3.9	5.4	4.0	5.1	1.15

<sup>a</sup>B. Monemar, Phys. Rev. B **12**, 5711 (1973).

is then to be superimposed to the charge distribution implied by the use of our dielectric function. If we suppose the transferred charge to be of the  $\delta$ -function type and centered at the ion sites, the corresponding potential can be written as follows:

$$V_T = -\sum_{\vec{r}_A} \frac{\Delta Z e^2}{|\vec{r} - \vec{r}_A|} + \sum_{\vec{r}_B} \frac{\Delta Z e^2}{|\vec{r} - \vec{r}_B|} \quad (8)$$

and can be then absorbed into the Coulombic parts of Eq. (7) by defining effective charges  $Z_A^* = Z_A + \Delta Z$  and  $Z_B^* = Z_B - \Delta Z$ . In Eq. (8) a positive value of  $\Delta Z$  corresponds to a charge transfer from A to B. It must be noted, however, that the use of the effective charges  $Z_A^*$  and  $Z_B^*$  in our calculations implies a screening of  $V_T$  too, which is certainly incorrect. Therefore the  $\Delta Z$  values which come out from the calculations and are

reported in the last column of Table II must be multiplied by some average value of the dielectric function in order to be compared, at least approximately, with other charge transfers, e.g., with those ones resulting from the Phillips<sup>10</sup> theory. This comparison can be made through the equation<sup>11</sup>

$$f_i^* = 1 - (Z - \Delta Z)/4e, \quad (9)$$

which connects the charge transferred from the cation site [accordingly in Eq. (9)  $Z = 3e$  for a III-V compound and so on] to the Phillips ionicity  $f_i$ . In Fig. 12 we report the Phillips  $f_i$  vs our  $f_i^*$ ; the latter have been computed from Eq. (9) by using the  $\Delta Z$  values of Table II multiplied for the values of  $\epsilon(q)$  at  $\vec{q} \equiv (2\pi/a)(1, 1, 1)$ ,

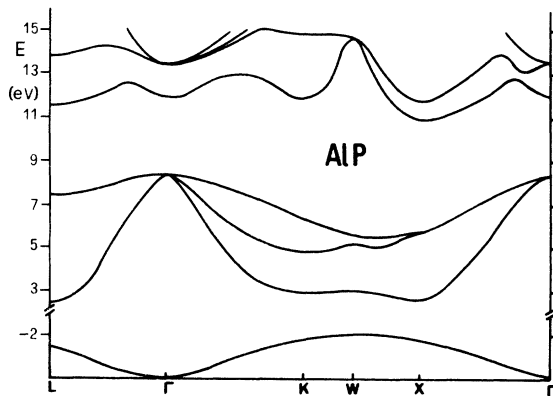


FIG. 9. Band structure of AlP.

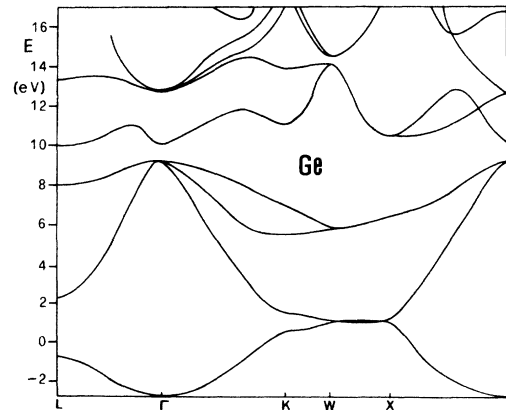


FIG. 10. Band structure of Ge.

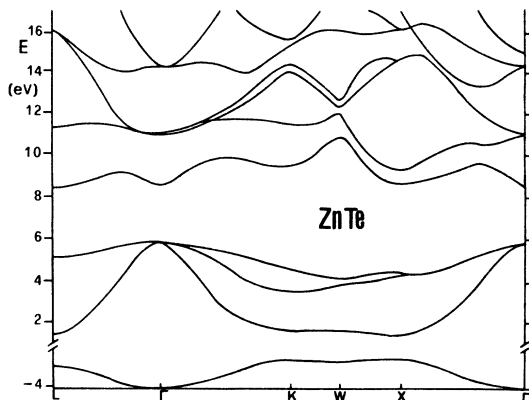
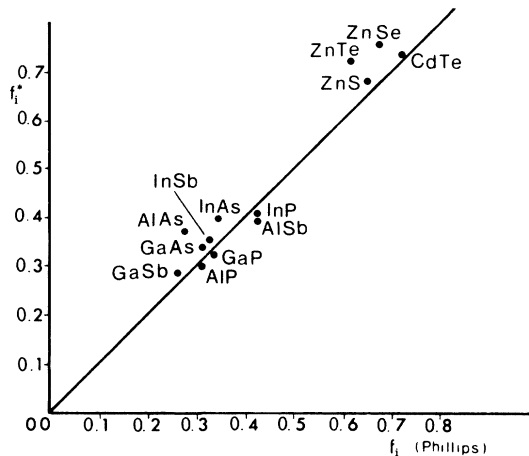


FIG. 11. Band structure of ZnTe.

which have been chosen, admittedly rather arbitrarily, as average values. It is rather gratifying, in spite of the approximations involved, that the best fit is obtained with a straight line of about unit slope. Accordingly it can be said that our fitting procedure for  $Z^*$  leads to an "experimental" determination of the ionicity.

#### IV. CONCLUSIONS

In summary the main points of our work are the following: (i) A general-model pseudopotential is introduced which has a simple analytical form in both direct and reciprocal space. (ii) The parameters of the model are determined by an extensive fitting of the optical properties of the groups IV, III-V, and II-VI semiconductors. (iii) The resulting potentials in real space seem quite reasonable and an interesting correspondence with the comparable experimental information is established. (iv) The charge-transfer effects which occur in heteropolar compounds are explicitly accounted for by defining effective valence charges  $Z^*$  in each particular compound. (v) In turn, the fitted values of  $Z^*$  may be regarded as giving information about the charge transfers that occur in the corresponding compounds. The overall agreement between Phillips and our ion-

FIG. 12.  $f_i^*$  values [see text, Eq. (9)] versus Phillips ionicities  $f_i$ .

icities is another support of the reliableness of our potentials.

A final comment should be made about the role the covalent bond plays in our model. As we have already remarked the neglect of nonlocality and energy-dependence effects was a consequence of our choice of forcing the wealth of nature into the narrow bounds of an analytical expression. Analogously we decided not to explicitly introduce into the Hamiltonian the Phillips bond charges, but rather to let their effect be indirectly accounted for through the fitting of the group-IV semiconductors. An additional excuse may perhaps be the small effect that the introduction of these charges would have on the band structures.

#### ACKNOWLEDGMENTS

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<sup>4</sup>V. Heine and I. V. Abarenkov, *Philos. Mag.* **9**, 451 (1964).

<sup>5</sup>D. R. Penn, *Phys. Rev.* **128**, 2093 (1962).

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<sup>9</sup>M. L. Cohen and T. K. Bergstresser, *Phys. Rev.* **141**, 789 (1966).

<sup>10</sup>J. C. Phillips, *Covalent Bonding in Crystals, Molecules and Polymers* (Chicago U.P., Chicago, Ill., 1970).

<sup>11</sup>J. C. Phillips, *Rev. Mod. Phys.* **42**, 317 (1970).