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Crystal Chemistry and Band Structures of the Group V Semimetals and the IV-VI Semiconductors

Abstract: Some simple facts regarding crystal structures and semiconducting vs semimetallic behavior of the Group V elements and the related Group IV-VI compounds are summarized. The simple chemical interpretation of these facts (based on three perpendicular p-bonding orbitals) is reviewed. This picture is reinterpreted in terms of a simple pseudopotential band model, which provides a deeper basis for understanding the simple chemical notions. The results of various band structure calculations are presented in detail in order to make explicit the direct relation between band and bond pictures as well as between crystal structures and semimetallic vs semiconducting behavior. The calculations also provide information as to probable locations of valence and conduction band edges.

1. *Crystal structures and electronic types*

In Table 1 we have summarized the structural information available for the Group V elements As, Sb, and Bi.[1-3] These crystallize in the so-called arsenic or A7 structure and are all semimetallic, by which one means that the pure substance is conducting at absolute zero with the carriers consisting of equal, small numbers of electrons and holes. We have also included in Table 1 the Group IV–VI intermetallic compounds PbS, PbSe, PbTe which have the NaCl structure and are semiconducting;[1] SnTe which is similar;[1,4] and GeTe which has the arsenic structure and is semimetallic.[4] The (SnGe)Te alloys[4] have a continuous range of solid solution, within which a change-over from the NaCl structure to the arsenic structure occurs at temperatures that decrease with increasing Sn content.

Within this group of related substances there are thus two structures, the NaCl associated with semiconductivity and the arsenic structure associated with semimetallic behavior. The two structures are themselves quite similar. If one ignores the difference between the Group IV and the Group VI elements, the NaCl structures of the IV–VI's become simple cubic. The structures of the Group V elements and of (GeSn)Te on the other hand are only "slightly" distorted from the simple cubic, as shown by the small deviations of the rhombohedral angles α from 60° and the internal coordinate u from 0.250.

We may summarize these facts by saying that in such substances having an average valence of five, the simple-

Table 1 **Crystal structure of the group V semimetals and some IV-VI compounds.**

	a (*trigonal*) Å	α	u	*a* (*cubic*) Å	*Ref.*
As	4.131	54° 10′	0.226	(5.564)	1
Sb	4.50661	57° 6.5′	0.233	(6.228)	2
Bi	4.7459	57° 14.2′	0.237	(6.568)	3
PbS	4.196	60°	0.25	5.935	1
PbSe	4.33	60°	0.25	6.122	1
PbTe	4.55	60°	0.25	6.439	1
SnTe	4.444	60°	0.25	6.285	1,4
GeTe	4.234	58° 15′	–	(5.988)	4

(SnGe)Te alloys show a continuous transformation from cubic to rhombohedral.[4] PbS, PbSe, PbTe, and SnTe all have the NaCl structure and are semiconductors. The others are semimetals.

α is the angle between two primitive translations of the face-centered rhombohedron. $2u$ is the minimum distance between adjacent atoms along the (111) direction in units of the rhombohedral diagonal.

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cubic structure is favored much as the diamond and closely related hexagonal structures are favored by substances having an average valence of four (Group IV elements, III–V and II–VI compounds). The simple cubic structure is apparently stabilized by the chemical difference of the IV and the VI component. When this chemical difference becomes too small, as in (GeSn)Te, or is absent, as in the Group V elements, the simple cubic structure becomes unstable with regard to a small structural change that consists of two independent distortions. One distortion is a small relative displacement of the two atoms within a face-centered-cubic unit cell along a body diagonal; the other is a small decrease in the rhombohedral angle from 60°. In the distorted structure, an overlap between valence and conduction bands leads to semimetallic behavior.

Further evidence for the instability of the simple-cubic structure is provided by the lattice-vibration spectra of these substances in so far as they are known. The distortion associated with the internal displacement may be regarded as the static version of the $\mathbf{k} = 0$ optical mode with polarization along the (111) direction. A tendency towards structural instability should manifest itself via an unusually low frequency of the corresponding normal mode. This is indeed the case for PbTe and PbS, for example, as shown by the unusually high values of the ionic contributions to the static dielectric constants.[5] Even after the distortion has taken place, as for example in Bi, the optical mode frequency at $\mathbf{k} = 0$ remains relatively low, as one sees from the measurements of Yarnell et al.[6] reported at this conference. The unusually low ratio C_{44}/C_{11} of the elastic constants in Bi[7,8] and even in PbS[8] provides a similar example for the instability against shear. It would be of great interest in this connection to measure the elastic constants and dielectric constants of (GeSn) Te alloys, particularly in the cubic-rhombohedral transition region.

This over-all structural similarity of the Group V elements and IV–VI compounds is paralleled by an over-all similarity of the gross features of the band structures. Cardona and Greenaway[9] have shown that similar peaks occur in the visible and ultraviolet reflectivities of the substances. Taken together, the optical and structural similarities justify a unified attempt to understand these substances. Such an attempt is made in the following sections.

2. Bond vs band theory

Structural regularities occur also for average valence 4, i.e., for elements of Group IV, for many III–V compounds, and for some II–VI compounds. In the former case the diamond structure is favored, in the latter two cases the zinc blende or a hexagonal analogue such as the wurtzite. All these structures involve tetrahedral coordination of the nearest neighbors. The conventional chemical interpretation is that the s^2p^2 configuration of the free atom is replaced by the sp^3 configuration in the crystal, giving rise to tetrahedral bonding by hybridized orbitals and hence tetrahedrally coordinated structures.

The above picture is of course enormously oversimplified. In fact, in all cases for which detailed band structures are known, they are much more accurately described as perturbed free-electron bands than as tight-binding bands, the pseudopotential matrix elements involved being significantly smaller than the spread of kinetic energy in the valence band (see, e.g., the results of Ref. 10 for Si and Ge.). However, despite the fact that the simple chemical picture appears to demand a tight-binding band scheme for it to be applicable in the crystal, close examination of the actual band structures shows that the chemical arguments can be carried over after suitable generalization, even for the perturbed free-electron case. Hence, we shall be quite justified in beginning our analysis of the substances of average valence 5 with the analogous chemical argument, which we do shortly.

The foundation of the analogy between the bond and band arguments is that for structures with a two-atom basis, with inversion centers at each atom, and with inversion centers between the two atoms in the unit cell, one can categorize the Bloch functions at the symmetry points as bonding-*s*, antibonding-*s*, bonding-*p*, antibonding-*p*, etc. The compatibility relations, which describe the connections of the various symmetry points along lines or planes of symmetry within the zone, then provide a rough but comparable classification of entire energy bands. Thus, one sees that in substances having the diamond or related structure the occupied valence bands, which are lowered by the crystal potential, are primarily of mixed bonding-*s* and bonding-*p* character, whereas the empty conduction bands, which are raised relative to the valence bands, are primarily of mixed antibonding-*s*, antibonding-*p*, and of still more complex character. As Kleinman and Phillips[11] have shown, the band picture even yields explicitly a pile-up of charge along the four nearest-neighbor directions.

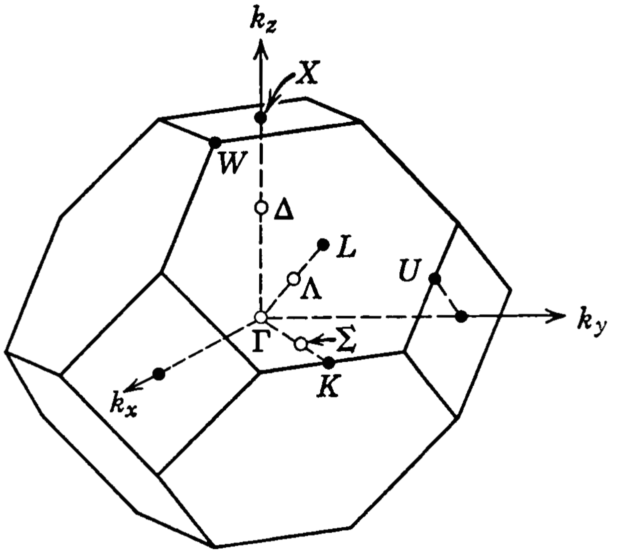
As one passes from the Group IV to the Group V elements, one can see from the atomic term values[12] that both the *s* and *p* shells are more tightly bound in the Group V elements with a somewhat increased separation of the *s* and *p* terms. The essential point is that the *s* electrons, being deeper lying, tend to participate less in the chemical behavior of the Group V elements than in that of the Group IV elements. A valence of 3, in fact, is quite common for the Group V elements As, Sb, and Bi, particularly Bi. The electronic configuration responsible for bonding is then p^3 in the simple chemical picture, which gives rise to 3 *p*-bonds at right angles and octahedral coordination. The simple cubic and related structures should thus be favored, as indeed they are.

In the following, we shall see that a band scheme based on perturbed free-electron energy bands corroborates in detail this simple chemical explanation. The previously discussed classification of Bloch functions, or orbitals, holds at points of sufficient symmetry, and the compatibility relations enable one to characterize in a gross way the individual bands as bonding-*s*, antibonding-*s*, bonding-*p*, antibonding-*p*, and mixtures or hybrids of these. We shall find that both the bonding and antibonding *s*-levels are occupied, whereas there is a fairly clear separation between (fully or almost fully) occupied bonding *p*-levels and unoccupied antibonding *p* and/or more complex levels. The *s*-levels thus do not contribute much to the bonding, whereas the *p*-levels dominate it, in agreement with the simple chemical picture.

3. Free electron bands in the face-centered-cubic zone. The program

(1) The energy bands of the substances of interest to us resemble free-electron bands because their pseudopotentials, while strong enough to cause insulating or semimetallic behavior, are not strong enough to eliminate the gross features of the free-electron bands. (2) The translational symmetry of the NaCl structure and of the arsenic structure also, if the deviation of the rhombohedral angle from 60° is ignored, is the same as that of the face-centered-cubic structure. (3) There are two atoms per unit cell in either structure contributing altogether 10 valence electrons. For these three reasons, we start by drawing the free-electron bands into the face-centered-cubic Brillouin zone with a Fermi energy corresponding to 10 electrons per unit cell. The latter is depicted in Fig. 1 together with the standard notation for the symmetry points;[13] the free electron bands and the Fermi level are depicted in Fig. 2.

Figure 1 **The Brillouin zone for the face-centered cubic structure, showing the standard notation for the symmetry points.[13]**



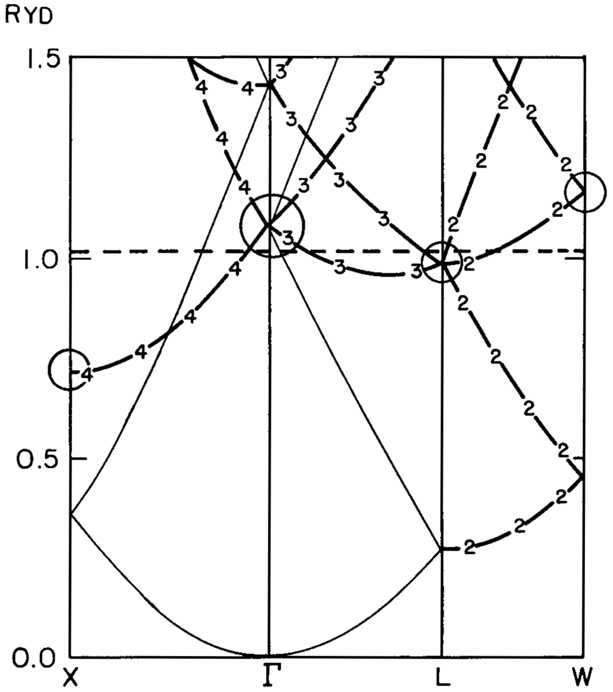


Figure 2 **The free-electron band energies in the face centered cubic zone; the Fermi energy corresponds to 10 electrons per unit cell.**

The occupation of levels which are relevant to the bonding and stability problems are summarized in Table 2. The effect, for example, of a simple-cubic crystal potential on these will be to split them into their bonding, antibonding, *s*, or *p* components. It should be noted, in addition, that the levels circled in Fig. 2 (8-fold at Γ, 4-fold at *X*, 6-fold at *L*, and 4-fold at *W*) are all within the range of the crystal potential about the Fermi energy. These points must all be regarded as potential positions of band edges, as indeed they have been by many earlier authors.

This is as much as can easily be learned from inspection of the free-electron bands. We turn now to an outline of the more realistic calculations which follow. The primary purpose of these calculations is to study the influence of the various departures from the simple-cubic structure upon the prominent features of the band structure. We assume throughout that the crystal pseudopotential is a superposition of spherically symmetric, screened, ion-core local pseudopotentials. Because all the structures considered possess a center of symmetry, the Fourier coefficients of the crystal pseudopotential can be expressed

Table 2 **Position of the relevant free electron levels.**

Symmetry point	Energy (Ryd) Below E_F		Above E_F	
X	2-fold	0.357		
	4-fold	0.714		
Γ	Single	0.000	8-fold	1.071
L	2-fold	0.268		
	6-fold	0.982		
W	4-fold	0.446	4-fold	1.160

$E_F = 1.012$

as the product of a real structure factor and the corresponding Fourier coefficient of the "atomic" pseudopotential. To illuminate the influence of structure, we use the same atomic pseudopotential for the simple cubic case, for the Group V elements, and for the average potential of the IV–VI compounds. In the latter case, there is in addition an "antisymmetric" component of the potential which has only two Fourier components taken to be nonzero, V_{111} and V_{311}. Table 3 lists all relevant Fourier components of the crystal pseudopotential used in the calculations reported here. The two different signs appearing in some of the coefficients of the simple-cubic potential correspond to choice of origin at a given atom (upper sign) or midway between two atoms along a (111) direction (lower sign). The values of "atomic" pseudopotential actually used were obtained by passing a smooth curve through the four pseudopotential coefficients determined for Ge by Brust,[10] $V_{111} = -0.23$ Ry, $V_{220} = 0.00$ Ry, $V_{311} = 0.06$ Ry, $V_{400} = 0.00$ Ry. These should not be grossly different from the correct ones, e.g., for As. The lattice parameters used throughout are those of arsenic, i.e., all the structures have the same atomic volume as does arsenic, and the As values of rhombohedral angle or internal displacement parameter are also used where appropriate.

A basis set of 89 plane waves was generated by adding to each **k** the 89 shortest reciprocal-lattice vectors. The resulting 89×89 secular equation was solved along various symmetry lines for the energy bands; the numerical calculations were carried out with the IBM 7094 system of the University of Chicago Computation Center. The set chosen was found to be large enough to give convergence adequate for our present purposes, e.g., the six lowest levels at Γ were convergent to within 10^{-3} Ry. Technical details of the calculations and group-theoretical considerations will be published elsewhere, as necessary.

We proceed now to discuss the results of these calculations for each of the following cases in turn: simple-cubic, IV–VI compounds, and an As structure. The latter case is taken in three steps: rhombohedral shear only; internal displacement only; and finally both together, giving the true As structure.

4. Energy bands in the simple cubic structure

The Brillouin zone of the simple-cubic structure[13] is shown in Fig. 3. However, the energy bands of the simple-cubic structure will be presented within the face-centered-cubic Brillouin zone. When the simple-cubic zone is folded into the face-centered-cubic zone, which has exactly half the volume of the former, the zone corner R coincides with the center of the zone, Γ; similarly, the middle point of the edge, M, goes into X, the center of the square face. It should be emphasized that the hexagonal face of the f.c.c. zone is not a true zone boundary for the s.c. structure. Consequently, if in the process of folding the s.c. Brillouin zone into the f.c.c. zone a point comes into coincidence with another point related to the former by a symmetry operation, sticking together of bands takes place. This is true, in particular, at L, W, and along the LW line, where all levels are even-fold degenerate.

We have two pentavalent atoms per f.c.c. unit cell; we must therefore doubly fill the equivalent of five bands in the f.c.c. zone. However, the sticking-together in pairs of the bands on the LW line of the hexagonal face allows only an even number of bands to be occupied in the entire vicinity of that face. This immediately implies metallic

Figure 3 **The Brillouin zone for the simple cubic structure, showing the standard notation for the symmetry points.**[13]

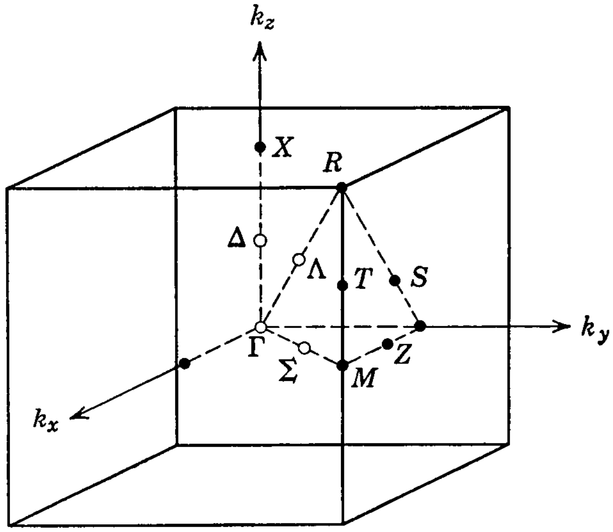


Table 3 **Fourier coefficients of the various pseudopotentials.**

	V(G) (Ryd)					
	Structure					
	S.c.	*Antisymmetric*		*Rhombohedral shear*	*Displaced f. c. c.*	*Arsenic*
G		I	II			
(111)	0	+0.093	+0.093	0	+0.099	+0.108
$(11\bar{1})$	0	+0.093	+0.093	0	−0.034	−0.032
(200)	−0.177	−0.177	−0.177	+0.176	+0.169	+0.168
(220)	+0.012	+0.012	+0.012	−0.018	+0.010	−0.015
$(2\bar{2}0)$	+0.012	+0.012	+0.012	+0.039	+0.012	+0.039
(311)	0	+0.025	+0.093	0	+0.039	+0.040
(222)	±0.042	+0.042	+0.042	−0.060	−0.026	−0.037
$(31\bar{1})$	0	+0.025	+0.093	0	−0.025	−0.023
$(3\bar{1}\bar{1})$	0	+0.025	+0.093	0	+0.009	+0.006
$(22\bar{2})$	±0.042	+0.042	+0.042	−0.032	−0.040	−0.031
(400)	+0.000	+0.000	+0.000	+0.000	+0.000	+0.000

Lattice parameters throughout are those for As or for related structures with the same atomic volume.

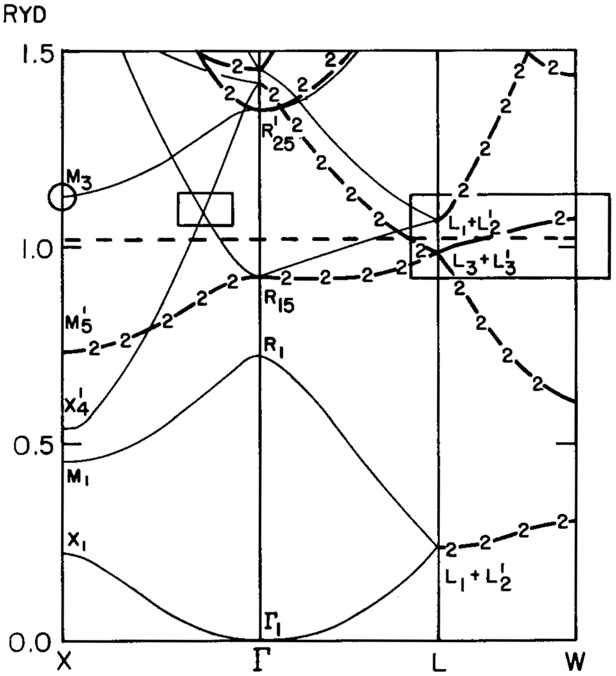
The two different signs appearing in some coefficients for the simple cubic lattice correspond to choice of origin at a given atom (upper sign) or midway between two atoms along the cube diagonal (lower sign).

character with a Fermi surface of area comparable to that of the f.c.c. zone. Further, the inequivalence of Γ and *R* and also of *X* and *M* gives rise to crossover degeneracies along the Γ*X* line which are also sufficient to yield metallic behavior. Similar arguments hold for other symmetry lines.

Clearly, one cannot argue for a pentavalent metal that the simple-cubic structure is stabilized by occupied bonding *p*-orbitals which are lowered in energy by the crystal potential relative to the unoccupied antibonding *p*-orbitals. In fact, the bonding and antibonding *p*-bands must both be partially occupied. This is an instance of a general theorem: no true covalent character can exist in metals.[14]

That the simple-cubic metal is not stabilized by covalent bonding of the sort discussed in Section 2 does not necessarily imply that the simple-cubic metal is of itself unstable. That instability tends to occur, at least for relatively weak crystal pseudopotentials, can be seen from the following argument. It has been shown[14,15] that the free energy of a metal can be decomposed exactly into a structure-independent and a structure-dependent part. The structure-dependent part in turn is a sum of pairwise interatomic interactions, a sum of triplet interactions, etc. The triplet and higher interactions are small if the pseudopotential is small. The free energy can then be

Figure 4 **The band energies for the simple cubic pseudopotential of Table 3.** *The boxes emphasize the important features of the curves.*



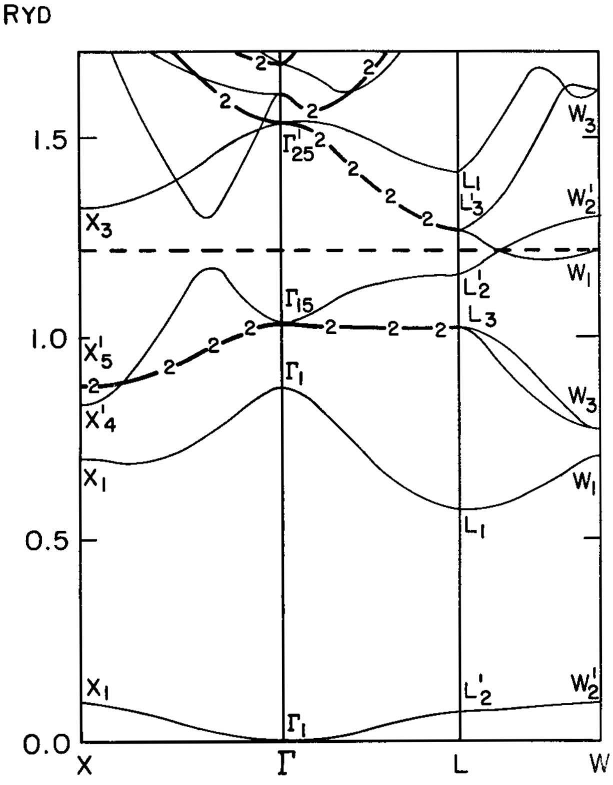
regarded as consisting of a structure-independent part and a sum of pairwise interatomic interactions. The pairwise interactions are central, and Born and his collaborators[16] showed long ago that the simple-cubic structure tends to be unstable for pairwise, central forces.

A detailed calculation of the band structure using the simple-cubic pseudopotential of Table 3 is shown in Fig. 4. It demonstrates quite explicitly the main features described so far. The features of the band structure which necessitate metallic behavior are displayed within boxes.

Despite the metallic character of our substance, it is very profitable to analyze the atomic and bonding character of the relevant wave functions at the symmetry points. The results of such an analysis are presented in Tables 4–7 for Γ, X, L, and W, respectively. The group-theoretical notations employed there and elsewhere in the paper are explained to some extent in the associated captions or footnotes; a more detailed discussion of the group theory will be presented in later papers, as necessary.

One can make the following observations regarding the contents of Fig. 4 and Tables 4–7:

Figure 5 **Band energies for the IV-VI compounds, corresponding to the antisymmetric pseudopotential labelled I in Table 3.** *The crossover degeneracy along LW gives rise to a structure borderline between semiconductor and semimetal.*



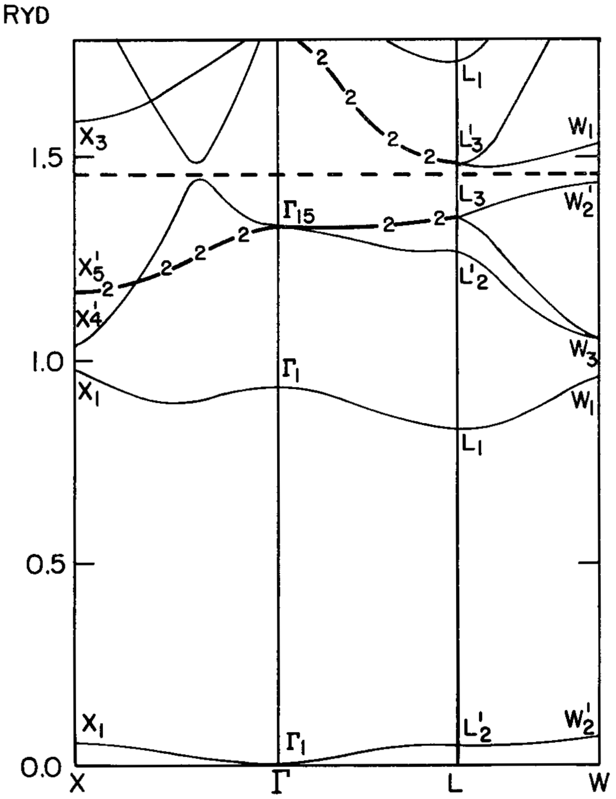


Figure 6 **Band energies for the IV-VI compounds, corresponding to the antisymmetric pseudopotential labelled II in Table 3.** The *semiconducting character of the structure is apparent.*

(1) No mixing of either atomic or bonding character occurs at Γ. The simple-cubic pseudopotential eliminates the free-electron degeneracies at Γ (e.g., the 8-fold level of Fig. 2 and Table 2) in such a way that the bonding-*s*, antibonding-*s*, and 3-fold bonding-*p* are the only levels remaining below the Fermi energy. Further changes of the potential or of the structure leave this feature essentially unchanged. Thus we see already in the simple-cubic structure the germ of the justification of the simple bonding arguments of Section 2.

(2) All relevant degeneracies are eliminated at X, but an M_3 (X_3) level is left close to and above the Fermi energy. The latter is circled in Fig. 4. Later changes in the potential leave the main features of X essentially unchanged, but this M_3 (X_3) level may possibly move below the Fermi energy, giving rise to electrons at X.

5. Energy bands for IV-VI compounds with the NaCl structure

To mimic the crystal potential of those IV–VI compounds with the NaCl structure we have added to the crystal potential various potentials which are antisymmetric about the point on the body diagonal midway between the two f.c.c. sublattices. The f.c.c. zone now becomes the correct Brillouin zone for the resulting crystal potential. The odd-odd-odd Fourier coefficients of the pseudopotential, zero in the simple-cubic structure, are now finite. We have considered various nonzero values of only the two lowest such Fourier coefficients, V_{111} and V_{311}. We summarize our general results and conclusions for four different cases we have computed, but in Table 3 and Figs. 5 and 6 we present only two cases explicitly.

The main effects to be noted are that the degeneracies at L, W and along the LW line are now lifted except for possible accidental degeneracies along LW. Similarly, the ΓX and the RM lines of the simple cubic zone are no longer distinguishable, and many previous "accidental

Table 4 **Atomic and bonding character of the wave functions at Γ.**

IV–VI *compounds*	*Simple cubic structure*	*Arsenic structure*	*Character*
Γ_1	$\Gamma_1 \leftrightarrow \Gamma_1$	Γ_1	s-bonding
Γ_1	$R_1 \leftrightarrow R_2'$	Γ_4	s-antibonding
Γ_{15}	$R_{15} \leftrightarrow R_{25}'$	$\Gamma_1\ p_\zeta$ $\Gamma_5\ p_\xi\ p_\eta$	(3) p-bonding
Γ_{25}'	$R_{25}' \leftrightarrow R_{15}$	$\Gamma_4\ d_{\xi\eta}$ $\Gamma_6\ d_{\xi\zeta} d_{\eta\zeta}$	(3) d-bonding
Γ_2'	$R_2' \leftrightarrow R_1$	Γ_1	f-bonding
Γ_{15}	$\Gamma_{15} \leftrightarrow \Gamma_{15}$	$\Gamma_4\ p_\zeta$ $\Gamma_6\ p_\xi\ p_\eta$	(3) p-antibonding
Γ_{12}	$\Gamma_{12} \leftrightarrow \Gamma_{12}$	Γ_5	(2) d-bonding
Γ_1	$\Gamma_1 \leftrightarrow \Gamma_1$	Γ_1	excited s-bonding

Symbols for the cubic representations are those of Bouckaert, Smoluchowski, and Wigner[13]. The two different notations for the simple cubic correspond to choosing the origin of coordinates at one atom (left) or at a point midway between two consecutive atoms along the cube diagonal (right). For the trigonal structure ζ represents the trigonal axis, ξ one of the 2-fold axes and η the perpendicular bisectrix. Identical representations in each case are connected by the lattice potential. *General remarks*: a) Simple cubic: There is no mixing either of bonding or of atomic character. b) IV–VI compounds: There is no hybridization of atomic character; there is mixing of bonding and antibonding states. c) Arsenic type structure: the crystal field splits all 3-fold levels into 2-fold and single levels. Both $s - p_\zeta$ hybridization and mixed bonding character occur. If the distortion from simple cubic is small, the hybridization is stronger than the bonding-antibonding mixing.

Table 5 **Atomic and bonding character of the wave functions at X.**

IV–VI *compounds*	*Simple cubic structure*	*Arsenic structure*	*Character*
X_1	$X_1 \leftrightarrow X_4'$	X_4	s; x, y-bonding z-antibonding
X_4'	$X_4' \leftrightarrow X_1$	X_1	p_z-bonding
X_1	$M_1 \leftrightarrow M_3$	X_1	s; x, y-antibonding z-bonding
X_3	$M_3 \leftrightarrow M_1$	X_1	(1) d_{xy}-bonding
X_5'	$M_5' \leftrightarrow M_5'$	$X_3\ p_\xi$ $X_4\ \alpha p_\eta + \beta p_\zeta$	p_x, p_y-bonding

Symbols for the cubic representations are those of Ref. 13. The two different notations for the simple cubic correspond to choosing the origin of coordinates at one atom (left) or at a point midway between two consecutive atoms along the cube diagonal (right). For the trigonal structure ζ represents the trigonal axis, ξ one of the two-fold axes and η the perpendicular bisectrix. Identical representations in each case are connected by the lattice potential. *General remarks*: a) Simple cubic: There is no *s-p* hybridization. Bonding and antibonding occur simultaneously for perpendicular directions in some representations, but no mixing occurs in a given bond. b) IV–VI compounds: There is no *s-p* hybridization; bonding and antibonding character are completely mixed. c) Arsenic type structure: *s-p* hybridization occur. There is no mixed character in a given bond; but simultaneous bonding and antibonding character occurs for perpendicular bonds.

Table 6 **Atomic and bonding character of the wave functions at L and T.**

IV–VI compounds	*Simple cubic structure*	*Arsenic structure*	*Character*			
			Atomic		*Bonding*	
			A	*B*		
L_1	$L_1 + L_2'$	T_1 L_1	s	p_{111}	partially bonding	Mixed for As
L_2'		T_2' L_4	p_{111}	s	partially bonding	
L_1	$L_1 + L_2'$	T_1 L_1	s	p_{111}	partially antibonding	Mixed for As
L_2'		T_2' L_4	p_{111}	s	partially antibonding	
L_3	$L_3 + L_3'$	T_3 $\left\{\begin{matrix}L_1\\L_2\end{matrix}\right\}$	d	$p_\perp$	partially bonding	Mixed for As
L_3'		T_3' $\left\{\begin{matrix}L_3\\L_4\end{matrix}\right\}$	$p_\perp$	d	partially bonding	

Symbols for the cubic representations are those of Ref. 13. Subindex 111 indicates the direction parallel to the corresponding ΓL or ΓT line; subindex $_\perp$ indicates the directions perpendicular to it. A and B indicate the two different interpenetrating f.c.c. lattices of the structure. Identical representations in each case are connected by the lattice potential. *General remarks*: a) Simple cubic: The bonding character is completely mixed. The atomic character can be preserved in individual atoms, while different characters exist for different atoms. b) IV–VI compounds: The degeneracies of the s.c. structure are lifted; the atomic character is necessarily preserved in each atom, but changes from atom to atom. c) Arsenic type structure: No clear pattern exists either for the atomic or for the bonding character.

Table 7 **Atomic and bonding character of the wave functions at W.**

IV–VI compounds	*Simple cubic lattice*	*Arsenic structure*	*Character*			
			Atomic		*Bonding*	
			A	*B*		
W_1	$W_1 + W_2' \leftrightarrow W_3$	W_1	s	p_z	bonding	Mixed for As
W_2'		W_2	p_z	s	bonding	
W_3	$W_3 \leftrightarrow W_1 + W_2'$	W_1 W_2	$p_x \leftrightarrow p_y$		bonding	
W_1	$W_1 + W_2' \leftrightarrow W_3$	W_1	s	p_z	antibonding	Mixed for As
W_2'		W_2	p_z	s	antibonding	
W_3	$W_3 \leftrightarrow W_1 + W_2'$	W_1 W_2	$p_x \leftrightarrow p_y$		excited bonding	

Symbols for the cubic representations are those of Ref. 13. The two different notations for the simple cubic correspond to choosing the origin of the coordinates at one atom (left) or at a point midway between two consecutive atoms along the cube diagonal (right). A and B indicate the two different interpenetrating f.c.c. lattices of the structure. Identical representations in each case are connected by the lattice potential. *General remarks*: These are the same for W here as they are for L and T in Table VI.

degeneracies" along ΓX in Fig. 4 are now removed, particularly the one shown in the box.

The detailed effects to be noted are:

(1) Small antisymmetric potentials do not lower the fifth level of W below the sixth level of L; the substance remains a metal.

(2) Larger antisymmetric potentials give rise to insulators in two different ways associated with the two different possible orderings of levels at W near E_F.

a) $W_2' > W_1$ (Fig. 5)

For any probable ordering of levels at L there is an accidental degeneracy along LW which is removed by spin-orbit coupling.

b) $W_2' < W_1$ (Fig. 6)

A clear cut separation between occupied valence and unoccupied conduction bands occurs even before spin-orbit coupling is added.

These two cases, illustrated in Figs. 5 and 6, are *bona fide* semiconductors, but neither of them should be considered a realistic representation of any particular IV–VI compound. However, it should be pointed out that minima of the conduction band and maxima of the valence band are probable in real substances along ΓX, along LW at L, or at W. It is also quite possible for the top of the valence band and the bottom of the conduction band to occur at the same point in $\mathbf{k}$-space in any of these cases.

From the results of Figs. 5 and 6 taken together with the results of Tables 4–7, the following inferences can be drawn:

(1) The antisymmetric potential still leaves each atom a center of symmetry; thus no hybridization occurs, i.e., the atomic character of the states is "pure" at points of sufficiently high symmetry in the zone.

(2) There is no longer a center of symmetry midway between atoms on different sublattices, and therefore the bonding and antibonding states of the simple cubic are mixed.

(3) This leads to increases in amplitudes of the wave functions at the sites of the Group VI elements over those at the sites of the Group IV elements and is responsible for the lifting of the degeneracies at L, W, and along the LW and ΓX lines.

(4) However, it is still possible to classify states as "bonding" and "antibonding" according to whether a node is absent or present along a nearest-neighbor line.

(5) In this way, the simple chemical-bond picture emerges as correct. The s-"bonding" and s-"antibonding" bands are both occupied, and stabilization of the crystal structure arises for strong enough antisymmetric potentials, from the occupation of the three p-"bonding" bands, while the three p-"antibonding" bands are unoccupied.

(6) It may be noted, incidently, that the case shown in Fig. 5 is unstable if spin-orbit splitting is neglected. This kind of instability is discussed in detail in Section 6(B).

6. Energy bands for Group V semimetals

In order to understand why both the rhombohedral shear and the internal displacement occur in the structures of the Group V semimetals, we calculate structures for : (A) — Simple-rhombohedral lattice; (B) — Displaced f.c.c. sublattices; and (C) — True As structure, in turn. We find that neither elementary distortion is separately sufficient to give a stable semimetallic structure. It should be noted in passing that values of deformation potentials can be obtained directly from calculations of this type.

• (A) — *Influence of rhombohedral shear*

The simple-rhombohedral structure remains metallic for pentavalent atoms because the translational symmetry is essentially the same as that of the simple-cubic. The 2-fold degeneracies in the hexagonal and pseudohexagonal faces of the Brillouin zone, Fig. 7, as well as the cross-over degeneracies along ΓX, ΓL, and ΓT, are not removed by the shear.

It is essential to note that the sign of the shear is such that the kinetic energies of those levels at T, the center of the hexagonal face, which are close to the Fermi energy

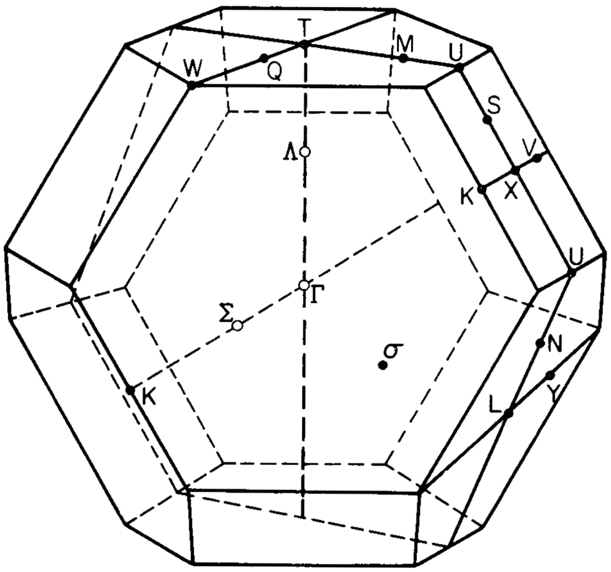


Figure 7 **The Brillouin zone for the face-centered rhombohedral structure showing the notation for the symmetry points, lines and planes.**[14]

are higher than the corresponding ones at L, the center of the pseudohexagonal face. This is illustrated clearly by the detailed calculations presented in Fig. 8, and will be of later importance. The potential used for these calculations is, as before, taken from Table 3.

Several minor points are apparent in the detailed calculations. There are crystal-field splittings of the 2-fold levels at X and the 2-fold level along ΓX. Similarly, the 4-fold level at L is split into two 2-fold levels, although the corresponding level at T, $T_3 + T_3'$, is not split. The sign of the crystal splitting of the 3-fold level Γ_{15} into the 2-fold level Γ_5 and the single level Γ_1 is such that $\Gamma_1 < \Gamma_5$.

The above results indicate that the shear is only of secondary importance in stabilizing structures of the Group V semimetals. Indeed, for shears as small as do occur it is hard to believe that the essential instability of the simple-cubic structure discussed at the end of Section 4 is at all alleviated.

• (B) — *Influence of the internal displacement*

We now consider the structure formed by the relative displacement, along a body diagonal, of the two interpenetrating f.c.c. sublattices of the simple-cubic structure. The translational symmetry is face-centered cubic so that the Brillouin zone has the shape of the f.c.c. zone of Fig. 1. However, the space group is identical to that of the true As structure, which is rhombohedral, necessitating a distinction between the hexagonal and pseudohexagonal faces, as in the zone of Fig. 7.[17] The internal displacement profoundly changes the structure factors in the Fourier coefficients of the pseudopotential (see Section 3). This gives rise to the fundamental differences observed between the second column (s.c.) and the sixth column (present structure) in Table 3. The resulting energy bands are shown in Fig. 9.

The 2-fold degeneracies in the hexagonal and pseudohexagonal faces are completely lifted by the internal displacement because the "f.c.c." zone is now appropriate to the translational symmetry, in contrast to the simple cubic or simple rhombohedral structures. Similarly most accidental degeneracies along ΓX and ΓL are well resolved. It is less so along ΓT. In this way the possibility of a semimetallic or insulating material arises.

The crystal-field splittings are similar to those of the simple-rhombohedral structure; one noteworthy difference is that the order of the Γ_1 Γ_5 pair, split from Γ_{15}, is reversed in the present case, with $\Gamma_5 < \Gamma_1$.

We come now to a somewhat involved argument which provides a possible basis for understanding the semimetallic nature of the Group V elements. The argument, at least at first, neglects spin-orbit effects, as these have not as yet been included in our detailed band-structure calculations. Detailed calculations with spin-orbit splitting are now underway and will be published elsewhere in due course. For the present we content ourselves with pointing out qualitatively where essential changes in the argument may occur.

To begin the argument, we note that the fifth and sixth levels at the corner W, a $W_1 W_2$ pair, seem always to be well split, with $W_1 > W_2$. This is associated with higher-order effects of the lower Fourier coefficients of the pseudopotential, which are similar for all substances considered here. We may anticipate that the results of a study of electron distribution, like that of Kleinman and Phillips[11] for diamond, will show this ordering and splitting to be associated with the formation of covalent bonds along

Figure 8 **Band energies for the simple rhombohedral structure corresponding to the pseudopotential labelled "rhombohedral shear" in Table 3.**

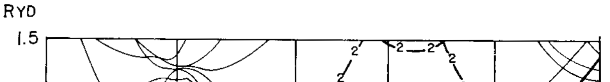
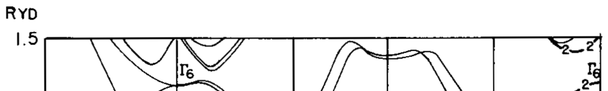


Figure 9 **Band energies for the displaced face-centered cubic sublattices corresponding to the pseudopotential of Table 3.** *The crossover degeneracy along the TW line has been boxed.*



the nearest-neighbor directions. The character of the wave functions corresponding to these levels given in Table 7 may be taken as tentative support for this view.

At the center T of the hexagonal face the order of levels near E_F, the Fermi energy, is T_2', $T_3 > T_1$, T_3'. The last two are the third, fourth, and fifth levels (T_3' is 2-fold). Again, this ordering is associated with properties of the pseudopotential which do not vary substantially from one material to another. We suspect here too that the order of the levels is tied up with the extent to which the corresponding wave functions can contribute effectively to the formation of a covalent bond.

That these two features of the band structure are fairly independent of the details of the potential has been established by two different pseudopotential calculations and by an approximately self-consistent orthogonalized-plane-wave calculation[18] for As, as well as by qualitative arguments.

As a consequence of the compatability relations along the TW line, T_1 is connected to W_1 and T_3 to W_2. Accordingly, there is an accidental crossover of levels which probably lies on the Fermi energy. This structure, borderline between insulator and semimetal, can be seen to be unstable, in the absence of spin-orbit splitting, by an argument much like that used to demonstrate the existence of the Jahn-Teller effect.[19] Stabilization can occur in two ways:

(1) By going into an insulator, which requires a radical change of the crystal structure or a very large change of the pseudopotential.

(2) By going into a semimetal and moving the crossover point off the Fermi energy.

In actual cases, a rhombohedral shear is, *post hoc*, the energetically most favorable structural change. The substance becomes a semimetal because the shear raises T_1 above E_F, as discussed previously in subsection (A), while some other levels, say L, or X, or both, go below E_F.

When the spin-orbit coupling is as large as it is in Bi, for example, the above argument should be taken with great care. The various representations of the single group are strongly mixed and the crossover degeneracies in general resolved.

(C) — *Energy bands in the arsenic structure*

Fig. 10 shows the results of a band structure calculation for the As structure in which the pseudopotential used is that shown in the last column of Table 3. The semimetallic character is now apparent. The most important effect of shear on the band structure for displaced f.c.c. sublattices, Fig. 9, is to raise the point of crossover degeneracy along the TW line above the Fermi energy giving rise to a stable semimetallic structure.

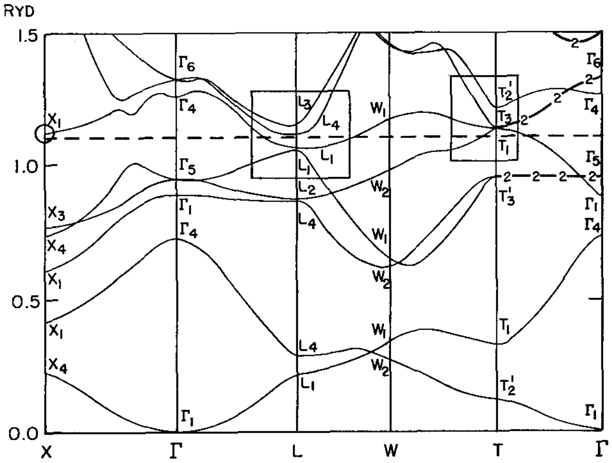


Figure 10 **Band energies for the arsenic type structure corresponding to the As pseudopotential of Table 3.** *This particular case corresponds to holes at T and electrons at L, but the proximity of the circled X level to the Fermi energy is apparent.*

It seems very probable, therefore, that in any substance of this group holes occur in the vicinity of T. The simplest case, which would occur for large spin-orbit coupling as in Bi, is the presence of one ellipsoidal piece of Fermi surface centered at T. For a smaller spin-orbit splitting, a more complex structure of the hole Fermi surface near T is likely, e.g., a fluted surface of 6-fold symmetry or even 6 equivalent "ellipsoids" with centers on the TW line and with no tilt. This complexity results from the detailed nature of the splitting of the crossover degeneracy by the spin-orbit coupling.

The location of the electron pieces of Fermi surface in the Brillouin zone, on the other hand, is less clear. For the case shown in Fig. 10, electrons occur at L, as is probably true for Bi. The complexity of the surfaces at L implied by the band structure of Fig. 10 would be somewhat mitigated by the spin-orbit coupling, particularly when it is as large as it is in Bi. In addition, fairly small changes in the pseudopotential can bring the X level circled in Fig. 10 below the Fermi energy, giving rise to electron ellipsoids at X with a tilt somewhat greater than 30°; this is perhaps what happens in As and Sb. It is even possible to have electrons both at L and at X, as probably occurs in some of the Bi-Sb alloys.

The discussion of the location of the band edges in the preceding two paragraphs is in substantial agreement with experimental evidence as we understand it. For detailed experimental references as well as various theoretical interpretations, see other papers of this conference.

Once again, the simple chemical picture can explain the gross features of the structure: two bands, predominantly s-bonding and s-antibonding are completely occupied; three bands with predominantly p-bonding character are almost completely occupied while the corresponding p-antibonding bands are almost completely unoccupied. Both mixing of bonding and antibonding character and s-p hybridization take place for this structure. The few holes in the fifth band and the few electrons in the sixth band are located at points in the Brillouin zone where the hybridization and the mixing of the bond character are greatest. Again this is in good agreement with the simple chemical arguments.

7. The (GeSn)Te alloys

We now have at hand in the discussions of Sections 5 and 6 a basis for understanding the cubic-rhombohedral transformation in GeTe and the (GeSn)Te alloy system.[4] In this system, the NaCl structure is stable above a transition temperature T_c, and a rhombohedral structure, which is almost certainly a direct analogue of the As structure, is stable below it. The transition temperature T_c decreases continuously with increasing Sn concentration from 700°K for pure GeTe to ~120°K for $Ge_{0.1}Sn_{0.9}Te$. For pure SnTe, T_c has been shown experimentally by Bierly, Muldawer, and Beckman[4] to be below 77°K, and their T_c vs composition curve extrapolates to the vicinity of 0°K. In sum, the NaCl structure of GeTe is unstable with respect to those same distortions which carry the simple cubic into the As structure of the Group V elements. The instability of the NaCl structure is continuously decreased by the addition of SnTe; the cubic structure may well become stable for pure SnTe.

We have proved that for a weak antisymmetric potential the substance remains metallic in the f.c.c. structure. It is then reasonable to associate structural instability with metallic character in precisely the same way we did for the simple-cubic Group V elements. Energy band arguments similar to those of Section VI, but not carried out in detail as done there, make it highly plausible that the distortions which stabilized the As structure will also stabilize a weakly antisymmetric IV–VI compound.

It remains to show that GeTe is indeed weakly antisymmetric and that substitution of Sn for Ge increases the magnitude of the antisymmetric potential. A rough measure of the strength of the atomic pseudopotentials out of which the crystal pseudopotential is built is given by the ionization potentials of the neutral atoms. The difference in the ionization potentials of the IV and VI elements of a IV–VI compound then gives a comparably rough measure of twice the magnitude of the antisymmetric potential. Table 8 lists the ionization potentials of the relevant Group IV and VI atoms. It is immediately apparent that the antisymmetric potential is probably a factor of two or so smaller in magnitude for pure GeTe than it is for pure SnTe or pure PbTe. This supports our contention that the antisymmetric potential of GeTe is insufficient to stabilize the NaCl structure.

Table 8 **Ionization Potentials (I.P.) of elements of Groups IV and VI.**

Group IV	*I.P.(eV)*	*Group VI*	*I.P.(eV)*
Ge	8.09	S	10.30
Sn	7.30	Se	9.70
Pb	7.38	Te	8.96

8. Acknowledgment

A number of the ideas presented here had their beginnings in discussions between one of us (M.H.C.) and E. I. Blount some years ago at Chicago. It was Blount who first pointed out in those discussions the importance of the essentially trivalent character of Bi for understanding the crystal chemistry and band structures of the semimetals.

We are also grateful to C. S. Barrett for crystallographic advice and information and to E. Burstein for discussions relating to the dielectric properties of the lead compounds.

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References

1. R. W. G. Wyckoff, *Crystal Structures*, Interscience Publishers, New York, 1960, Vol. 1.
2. C. S. Barrett, P. Cucka, and K. Haefner, *Acta Cryst.* **16**, 451 (1963).
3. P. Cucka and C. S. Barrett, *Acta Cryst.* **15**, 865 (1962).
4. T. N. Bierly, L. Muldawer, and O. Beckman, *Acta Met.* **11**, 447 (1963).
5. For the refractive indices see D. G. Avery, *Proc. Phys. Soc.* **B64**, 1087 (1951); **B65**, 425 (1952); **B66**, 133 (1953); **B67**, 2 (1954). For the static dielectric constant of PbTe see Y. Kanai and K. Shohno, *Japan. J. Phys.* **2**, 6 (1963). In the case of PbS, the transverse $\mathbf{k} = 0$ optical mode frequency has been measured directly and the static dielectric constant estimated to be ~ 160 by J. Zemel, private communication to E. Burstein. We are greatly indebted to Prof. Burstein for stimulating discussions of these points.
6. T. L. Yarnell, T. L. Warren, R. G. Wenzel, and S. H. Koenig, *IBM Journal* **8**, 234 (1964). (This conference.)
7. Y. Eckstein, A. W. Lawson, and D. H. Reneker, *J. Appl. Phys.* **31**, 1534 (1960).
8. H. B. Huntington, *Solid State Physics* vol. 7, Academic Press, New York, 1958, pp. 276, 282.

9. M. Cardona and D. L. Greenaway, *Phys. Rev.* (to be published).
10. D. Brust, *Phys. Rev.* (to be published) and earlier references quoted there.
11. L. Kleinman and J. C. Phillips, *Phys. Rev.* **125**, 819 (1962).
12. See e.g. J. C. Slater, *Quantum Theory of Atomic Structure*, McGraw-Hill Co., Inc., New York, 1960, Vol. 1, p. 206, Table 8-2.
13. L. B. Bouckaert, R. Smoluchowski, and E. Wigner, *Phys. Rev.* **50**, 58 (1936).
14. M. H. Cohen, *J. Phys. Rad.* **23**, 643 (1962), and further unpublished work.
15. M. H. Cohen, *Proceedings of the Special Session on Concentrated Solid Solutions*, the Cleveland meeting of the ASM, October, 1963. (To be published.)
16. R. D. Misra, *Proc. Cambridge Phil. Soc.* **36**, 173 (1940); M. Born and M. Bradburn, *Proc. Cambridge Phil. Soc.* **39**. 104 (1943); M. Bradburn, *Proc. Cambridge Phil. Soc.* **39**, 113 (1943).
17. M. H. Cohen, *Phys. Rev.* **121**, 387 (1961).
18. Stuart Golin, to be published.
19. See for instance, C. A. Coulson and J. T. Lewis in *Quantum Theory*, edited by D. R. Bates, Academic Press, New York and London, 1962, Vol. 2, p. 201 ff.

Discussion

G. E. Smith: Are the two E vs k lines above the electron band (Fig. 10) in bismuth sufficiently close to influence the character of the electron band near the Fermi level?

M. H. Cohen: Those are in fact quite widely separated in the case of bismuth, with a spin-orbit splitting of about 1.5 volts. These calculations do not include spin-orbit splitting. But if one looks at the details of the structure, certain levels can't cross even though one has spin-orbit splitting; so that one can get a situation with only two levels close to the Fermi level for large spin-orbit splitting. In the case of arsenic the spin-orbit splitting is comparable to the level separation one estimates from the germanium pseudopotential. Stuart Golin has calculated an almost self-consistent OPW band structure for arsenic ("almost" in the sense that it is a superposition of atomic potentials). He finds that X comes down and the band structure around L is changed according to the details of the pseudopotential. So the answer is that there probably aren't other bands near it.

Peter Lee: I wish to report some preliminary results of band structure calculations on the series of compounds Mg_2X, where X is Si, Ge, Sn or Pb. These compounds show semiconducting behavior when X is Si, Ge or Sn and metallic behavior when X is Pb. The method used is that of pseudopotentials and results have so far been obtained for the cases Mg_2Si and Mg_2Ge. The appropriate Brillouin zone is that for the face-centered-cubic lattice. The results show in the case of Mg_2Si a band gap of about 1 eV. The position of the maximum of the valence band is found to be at $k = 0$, and the bottom of the conduction band at the zone face X. The results for Mg_2Ge are similar.

Further calculations are being carried out for Mg_2Sn and Mg_2Pb and on a model for the alloy system $Mg_2(Sn)_x(Pb)_{1-x}$. The method is useful since it permits the determination of the energy levels in terms of a few Fourier coefficients of pseudopotential and the relative positions of the bands may be studied directly by varying these coefficients.