orientation of H_0 with respect to the molecular axes (θ_H) can tell us the type of motion involved. This sort of information is quite analogous to the line-narrowing studies of molecular rotation done in conventional resonance.

B. Intermolecular Contributions

It is a straightforward matter to generalize Eq. (87) to take into account the intermolecular contribution. The labels i and j then refer to atoms not necessarily in the same molecule. We get a particularly simple form when the molecules can only jump about a 2-fold axis perpendicular to the internuclear line within the molecule, as when the protons of a water molecule exchange positions. Let us use the labels i, q, and r to label the *positions* of the nuclei which will be involved in the dipole sum. We let q and r stand for the two sites within a molecule whose nuclei exchange positions. We assume the other nuclei i do not move when nuclei at q and r interchange. Then we get

$$\frac{1}{T_c}=\frac{2}{\tau}\sum_i(A_{iq}-A_{ir})^2/\sum_i(A_{iq}+A_{ir}^2)\,, \tag{92}$$

where

$$A_{iq}=(1/r_{iq}^3)(3\cos^2\theta_{iq}-1)\,. \tag{93}$$

It is important to realize that Eq. (92) holds true as long as the various dipolar and Zeeman terms can exchange energy in the rotating reference frame. To the extent that this holds true, Eq. (92) automatically takes care of splittings of the resonance into several components, as when one has a Pake doublet in a water molecule.

ACKNOWLEDGMENTS

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Electronic Structure of Magnesium Silicide and Magnesium Germanide*

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Pseudopotentials previously calculated for metallic magnesium and semiconductors silicon and germanium are used to calculate the electronic energy-band spectra of magnesium silicide and magnesium germanide. Results are obtained for the energy gap and the positions of the valence-band maximum and conduction-band minimum which are in agreement with what is known experimentally about these substances. The use of the energy levels determined is discussed in interpreting ultraviolet reflectance spectra of these compounds. Finally, on the basis of the present calculations, some speculations are made about the nature of the electron and hole energy surfaces in the semimetallic region of the alloy system $Mg_2\,(Sn)_x\,(Pb)_{1-x}$.

I. INTRODUCTION

THE series of compounds Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb have the interesting property that while the first three members of the series are semiconductors, Mg_2Pb has electrical properties which are definitely of a metallic nature. The transition appears to be smooth and occurs somewhere in the alloy system $Mg_2(Sn)_x(Pb)_{1-x}$. The present work reports results of band-structure calculations on the first two members of the series. These have been carried out using pseudopotentials which were originally evaluated for the elements separately. Although there has been some discussion of the usefulness of these pseudopotentials, the present calculation is, as far as the author knows, the first one for a compound which takes over the pseudopotentials determined separately for the various constituent elements, one metallic and one insulating. The approximations involved in doing this are discussed in the text.

Experimental measurements of the electrical properties have been made on polycrystalline samples of all members of the series by Busch and Winkler[1,2] and of the resistivity and Hall effect on single crystals of magnesium silicide and germanide by Danielson and co-workers.[3–5] Piezoresistance measurements of magnesium silicide[6] have been made and the position of the bottom of the conduction band determined from

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* Work supported by the National Science Foundation and also by a general grant to the Institute for the Study of Metals by the Advanced Research Projects Agency.

[1] G. Busch and U. Winkler, Physica **20**, 1067 (1958).

[2] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).

[3] R. G. Morris, R. D. Redin, and G. C. Danielson, Phys. Rev. **109**, 1909 (1958).

[4] R. D. Redin, R. G. Morris, and G. C. Danielson, Phys. Rev. **109**, 1916 (1958).

[5] M. W. Heller and G. C. Danielson, in *Proceedings of the International Conference on Semiconductor Physics*, (Czechoslovakian Academy of Sciences, Prague, 1961), p. 881.

[6] W. B. Whitten and G. C. Danielson (to be published).

these. The agreement between these experimental results and the present calculations is good enough to indicate that the calculated band structure can be used as a basis for interpreting further experimental results for the two compounds.

II. STRUCTURE

The series of compounds with the chemical formula Mg_2X where X is silicon, germanium, tin or lead, all crystallize with the calcium fluoride structure. The positions of the atoms in the unit cell are shown in Fig. 1. The electropositive magnesium atoms occupy the sites which electronegative fluorine atoms occupy in calcium fluoride, while the electronegative group IV metals occupy the calcium atom sites. The lattice has face-centered cubic translational symmetry and the appropriate Brillouin zone is given for reference purposes in Fig. 2. The values of the lattice parameters were taken to be:

$$Mg_2Si: a = 12.077 \text{ atomic units,}$$
$$Mg_2Ge: a = 12.053 \text{ atomic units,}$$
$$Mg_2Sn: a = 12.783 \text{ atomic units,}$$
$$Mg_2Pb: a = 12.918 \text{ atomic units.}$$

From the band picture point of view it is most convenient to regard the four *s* electrons from the magnesium atoms and the four *s* and *p* electrons from the group IVb metal as making up the eight electrons per unit cell which go into the valence band. The irreducible representations which classify the energy levels both within the Brillouin zone and on the surface faces are those for the face-centered cubic lattice.

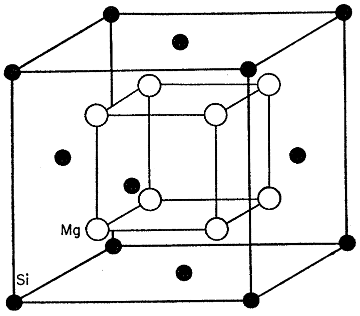

FIG. 1. Atomic arrangement in Mg_2Si.

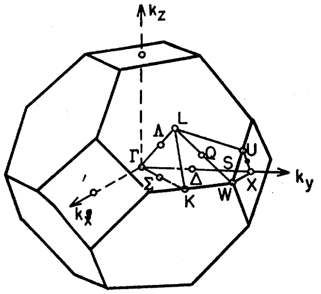

FIG. 2. Brillouin zone for face-centered cubic lattice.

III. THE ENERGY-BAND CALCULATIONS

The method of calculating the energy bands is the simple one of expanding the wave function in terms of a finite sum of plane waves and diagonalizing the resulting Hamiltonian matrix. The convergence of the eigenvalues is checked directly by introducing extra plane waves into the expansion and recomputing the eigenvalues. If this expansion is used with a crystal Hamiltonian which contains the atomic-like potential around the atoms, then the convergence of such a series is known to be poor. However, recent work[7] has shown there is almost complete cancellation of the large negative potential energy that a valence electron sees in the core region by its own large positive kinetic energy. The details of the cancellation are given in the previous reference. Because of this cancellation, the wave equation may be written:

$$(T+V+V_R)\varphi = E\varphi.$$

The term $(V+V_R)$ is the net, weak pseudopotential and because of the cancellation of V by V_R, the pseudowave function φ is then well approximated by an expansion in plane waves.

In the present calculation, convenient pseudopotentials were chosen from the start. For the atoms of silicon and germanium these were taken from the work of Brust,[8] and for magnesium from the work of Harrison.[9] From Brust's data, which is a set of Fourier coefficients of pseudopotential, defined only for the first few reciprocal lattice vectors in crystalline silicon and germanium, and chosen to fit the experimentally determined band structure, a smooth curve was drawn so that Fourier coefficients for any other values of the lattice parameters could be obtained. The restriction imposed by Brust that for the larger reciprocal lattice vectors the Fourier coefficients should vanish was retained. From Harrison's work, a graph of a similar function for magnesium was obtained from $|\mathbf{k}| = 0$ out to $|\mathbf{k}| = 2k_F$, where k_F is the Fermi momentum for magnesium. From this point a smooth exponential tail was fitted onto the graph so that the function went effectively to zero at about $|\mathbf{k}| = 2.4$ atomic units. Thus both these curves are determined for the atoms in the form of crystals of the elements. The present method thus makes the approximation of assuming that these atoms give rise to a similar pseudopotential when they exist in compounds, and therefore the only changes in the values of the Fourier coefficients of pseudopotential are due to changes in the lattice parameter. It is recognized here that while this may be true for the contributions to the pseudopotential from the core states, any part due to self-consistent adjustments of

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[7] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[8] D. Brust (to be published).

[9] W. A. Harrison, General Electric Research Laboratory, Report No. 63-RL-(3322M), May 1963 (unpublished).

the valence-band charge density must alter from one environment to another, the changes being smaller where the bonding of the valence electrons is similar from one crystal to another. Several other approximations are involved in using the above form of the pseudopotential. It is well known[10,11] that the actual pseudopotential, written above as $(V+V_R)$ is a nonlocal function, the repulsive term V_R being defined by a complicated integral. The errors involved in replacing this complicated function by the simpler and more manageable one used above have been considered in some detail by Cohen and Heine.[7] Firstly, it is to be expected that the pseudopotentials used above, as originally defined by Brust and Harrison, will only be good for calculating energies which lie near the free-electron Fermi energy for the magnesium lattice and also for energies which are close to the band-edge energies in silicon and germanium. Strictly speaking, this puts inconsistent demands on the results for the present problem. However, the Fermi energy for magnesium is 0.69 Ry, the corresponding figure in silicon and germanium is about 0.8 Ry, and the interesting levels in the present compounds turn out to be in the range 0.7–0.8 Ry measured from the bottom of the valence band. From this point of view, the situation seems quite favorable. A further limitation is that in reducing the pseudopotential to a simpler form, it is implicit that a different function should be used to calculate levels of different symmetries. In the present calculation, it turns out that the state at the top of the valence band in both compounds, has a wave function whose symmetry is *p*-like about the origin (a silicon or germanium atom). There are no other contenders for this position. The lowest state in the conduction band, however, has a leading term of *s*-like symmetry. The calculations indicate that other states which might be the bottom of the conduction band also have leading terms of *s*-like symmetry. Thus in treating these states the calculation is consistent, although inconsistency occurs in using the same pseudopotential for the top of the valence band and could well lead to large errors in the value of the energy difference between levels of different symmetry from which the energy gap arises in the present problem. Experience has shown that *s*-*p* differences in the pseudopotential are smallest in the third row of the periodic table, which contains both magnesium and silicon.

TABLE I. Comparison of calculated and experimentally measured properties.

	ΔE_{calc}(eV)	$\Delta E_{\text{Ex.}}$	$(m_{\parallel}/m_0)_{\text{calc}}$	$(m_{\perp}/m_0)_{\text{calc}}$
Mg_2Si	1.3	0.77[a]	0.69	0.25
Mg_2Ge	1.6	0.74[a]	0.63	0.25

Values for the effective masses of *n*-type compounds have been given as[b]:

Mg_2Si $m_n=0.46$
Mg_2Ge $m_n=0.18$

[a] See Refs. 1 and 2.

[b] See Refs. 3 and 4. The values for $\Delta E_{\text{Ex.}}$ given by these workers differ somewhat from those given above, but not significantly for the present comparison.

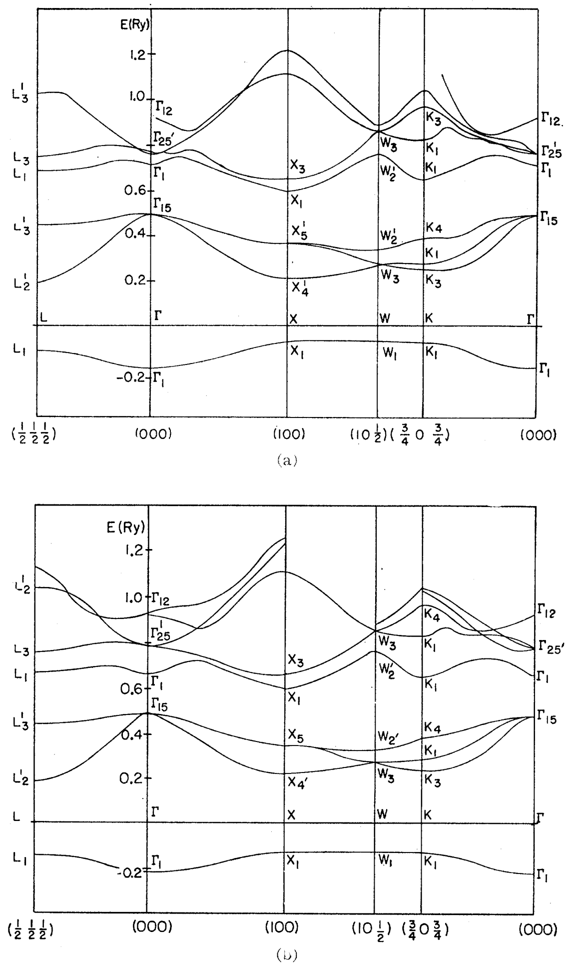

FIG. 3. (a) Energy bands for Mg_2Si. (b) Energy bands for Mg_2Ge.

The results obtained for the band structures of magnesium silicide and magnesium germanide by the above method are shown in Fig. 3. The particular results shown were obtained with 51 plane waves in the expansion of the wave function. Calculations with 89 plane waves have been made for the symmetry points and these show no major changes in the band structure from that given in the figures. The energy matrix was diagonalized directly on the University of Chicago IBM-7094 computer system. Representations of the groups of *k* were used to classify the energy levels from the coefficients of the plane waves, although in most cases this could be done by inspection. The results are very similar for the two compounds. The top of the

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[10] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[11] E. Antoncik, Phys. Chem. Solids **10**, 314 (1959).

valence band is at the origin and is a Γ_{15} level in each case. The over-all nature of the valence band is very similar to other semiconductors which have face-centered cubic translational symmetry and eight electrons per unit cell to go into this band. This is found not to change very much both in the group IV semiconductors and the III-V compounds. In the present calculation, the valence band is again found to be very stable to changes in the pseudopotential. The bottom of the conduction band is found to be at the zone face in the [100] direction, and is a level of type X_1 in both cases. The presence of the level X_3 just above X_1 is somewhat disturbing. The leading term in the expansion of the wave function for level X_3 is *d*-like. Clearly this level is not treated very accurately by the present method. The position of this level is therefore not well known from the present calculation.

Calculated values for the energy gaps and effective mass components for electrons at the bottom of the conduction bands are given in Table I along with experimentally measured values.

TABLE II. Bonding nature of some levels in magnesium silicide.

	Si-Mg	Si-Si	Expansion round Si	Expansion round Mg
Γ_{15}	Bonding	Antibonding	p	p
Γ_1	Antibonding	Antibonding	s	s
X_5'	Bonding	Antibonding	p	p
X_1	Bonding	Antibonding	s	p
X_3	Bonding	Bonding	d	s
L_3'	Nonbinding	Bonding	p	$\cdots$
L_1	Bonding	Antibonding	s	s
L_2	Nonbonding	Nonbinding	d	$\cdots$

Because no new parameters have been added to this calculation, the values for the energy gap in these substances may be considered to be in good agreement with experiment. The position of the bottom of the conduction band is in agreement with that found[6] from measurements of piezoresistance in magnesium silicide.

The bonding or antibonding nature of the wave functions between a silicon atom and its nearest neighbor magnesium and silicon atoms is of some interst and this is shown in Table II. Also shown are the leading terms in a spherical harmonic expansion of the wave function about a silicon and a magnesium nucleus. The term "nonbonding" for the functions L_3' and L_3 is used to indicate that the direction lies in a nodal plane of the wave function. The tendency of bonding orbitals, with low values of angular momentum, to form the states in the valence band can be noted from the table.

The complete calculation of course has to include relativistic corrections to the energies. Since the pseudopotentials used for silicon and germanium were empirically determined, the difficulties associated with including these corrections are discussed later.

TABLE III. Calculated optical transitions and Van Hove singularities in magnesium silicide and magensium germanide.

Transition	Type of singularity Mg_2Si:Mg_2Ge		Energy (eV) Mg_2Si:Mg_2Ge	
$\Gamma_{15} \rightarrow \Gamma_1$	M_0	M_0	2.84	2.51
$X_5' \rightarrow X_1$	M_0	M_0	3.10	3.26
$L_3' \rightarrow L_1$	M_0	M_0	3.18	3.20
$\Lambda_3 \rightarrow \Lambda_1$	M_1	M_1	3.28	3.28
$K_4 \rightarrow K_1$	M_0	M_0	3.47	3.68
$\Gamma_{15} \rightarrow \Gamma_{25}'$	$\cdots$	$\cdots$	3.67	4.20
$\Delta_5 \rightarrow \Delta_1$	M_1	M_1	3.75	4.08
$X_5' \rightarrow X_3$	M_0	M_0	3.77	4.04
$\Sigma_4 \rightarrow \Sigma_1$	M_1	M_1	3.81	3.96
$L_3' \rightarrow L_3$	M_2	M_2	4.10	4.40
$\Delta_5 \rightarrow \Delta_2'$	M_3	M_3	4.30	4.27
$\Lambda_3 \rightarrow \Lambda_3$	M_3	M_3	4.37	4.69

IV. OPTICAL PROPERTIES

Recent work[12] has shown that many details of the electronic band structure in different types of solids may be obtained by critically studying the structure of the imaginary part of the complex dielectric constant function $\epsilon_2(\omega)$. This is obtained experimentally from reflectance measurements in the energy range between about 1 and 10 eV. It can be shown (see for example, Ref. 12) that the analytic singularities in the expression for $\epsilon_2(\omega)$ arise from those of the joint density-of-states function:

$$\frac{dN_{ij}}{dE} \sim \int \frac{1}{|\nabla_k E_{ij}|} dS_k ,$$

where $E_{ij}(\mathbf{k}) = E_j(\mathbf{k}) - E_i(\mathbf{k})$ is the difference in energy between conduction- and valence-band states. The effect of the singularities in dN_{ij}/dE due to $|\nabla_k E_{ij}| = 0$ has been studied in detail.[13,14] The Van Hove singularities in $\epsilon_2(\omega)$ may be deduced from a knowledge of the critical points in $\mathbf{k}$ space, that is points in $\mathbf{k}$ space for which $|\nabla_k E_{ij}| = 0$. These are obtained from the band-structure calculations for the allowed transitions. The different mathematical behavior of dN_{ij}/dE near the critical points can give rise to four different kinds of singularities. These are either thresholds or saddle-points and are shown in Fig. 4. The dipole allowed transitions at the critical points in magnesium silicide and magnesium germanide are listed in Table III for

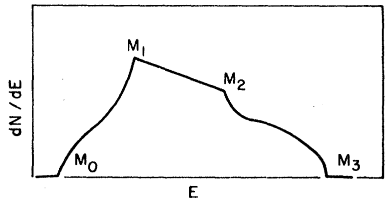

FIG. 4. Van Hove singularities in the density of states of $E(\mathbf{k})$ ranging over a three-dimensional Brillouin zone.

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[12] J. C. Phillips, Phys. Rev. **125**, 1931 (1962); **133**, A452 (1964); Phys. Rev. Letters **12**, 142 (1964).

[13] L. Van Hove, Phys. Rev. **89**, 1189 (1953).

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

transitions to the first two conduction bands. The type of edge expected (Fig. 4) is denoted as well as the energy for the transition calculated from the present band-structure results.

A further factor affecting the interband transitions is the oscillator strength:

$$f_{ij}(\mathbf{k}) \sim |\langle \mathbf{k}_j | p | \mathbf{k}_i \rangle|^2 / (E_j - E_i).$$

The square of the matrix element has been examined in some detail for the case of silicon by Brust.[8] This is found to be roughly constant throughout the zone, varying by less than a factor of 2. If it is assumed that the same results apply in the present case, then the reflectance spectra will be directly interpretable in terms of singularities shown in Table III. Experimental measurements of the reflectance spectra have not yet been made and it is interesting to speculate a little on the basis of the above results. In particular the transition $\Lambda_3 \rightarrow \Lambda_1$, which shows up as the leading peak in $\epsilon_2(\omega)$ for germanium, has the same type of singularity (M_1) in both cases. Further, in both cases the energy contours for $E_j - E_i$ around this singularity indicate a high joint density of states and hence a high contribution in each case. This feature in $\epsilon_2(\omega)$ in germanium might thus be expected to be reproduced for the present compounds. Further comparisons are increasingly difficult due to the different nature of the singularities for particular transitions. Phillips[12] has pointed out the insensitivity of reflectance spectra to changes in atomic composition in the diamond and zincblende structures. This suggests a scheme based on the nearly free-electron approximation, where the dominant features would be determined by the shape of the Brillouin zone. Such a scheme cannot be neglected for the present compounds and a comparison of their reflectance spectra with those of the diamond and zincblende structures is an obvious first step in interpreting them once they have been measured. It will be interesting to see if such a scheme is still a good one for the present case where there are three atoms per unit cell.

V. CONCLUSION

The calculation reported here shows that a pseudopotential determined for an atom in one crystal environment can be carried over and used to determine energy levels in another crystal under certain suitable conditions. These are:

(a) The energy levels to be computed must lie within the same range on the unperturbed free-electron picture for each lattice.

(b) The contributions to the pseudopotential from the self-consistent valence-band charge do not differ appreciably from one crystal to the other.

(c) Proper consideration is given to the errors introduced by the more general problem of using a local form of pseudopotential.

Conditions (a) and (b) are seen to be fairly well satisfied in the present problem and some indication has been given as to which energy levels are expected to be badly described due to errors introduced by (c).

A full band structure calculation should of course include relativistic effects in the results. Because of the empirical nature of the silicon and germanium pseudopotentials, this has not been done in the present case. The whole aim of the calculation has been to extract as much information as possible to form a basis for interpretating such experimental results as ultraviolet reflectance measurements and studies of transport properties so that these may be used to set up the correct energy level scheme. However, work is going ahead to see if the relativistic shifts in the levels can be responsible for making the conduction and valence bands overlap in order to account for the transition from semiconductor to semimetal in the alloy series $\mathrm{Mg}_2\ (\mathrm{Sn})_x\ (\mathrm{Pb})_{1-x}$ as x decreases.

The present calculations have shown what changes are necessary in the pseudopotential to produce this transition. These indicate that overlap will occur to produce hole surfaces at $\mathbf{k}=[000]$ and electron surfaces at $\mathbf{k}=[100]$. More detailed calculations of the relativistic effects are being carried out to determine if these would move the bottom of the conduction band to another point in the Brillouin zone and thus produce a different configuration for the electron surfaces.

ACKNOWLEDGMENTS

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