It should be noted that the $Mn^{4+}-O$ bond has been assumed equal in length to the $Mn^{3+}-O$ bond with covalent character. This is a fair approximation if the covalent character of the $Mn^{4+}-O$ bond is less than that in the $Mn^{3+}-O$ bond; the general decrease in T_0 with added Mn^{4+} content is consistent with this hypothesis.

It is concluded, therefore, that at least in the manganites $[La,M(II)]MnO_3$ the theory of superexchange is inadequate whereas the concepts of covalence and semicovalent exchange offer a consistent model for explaining complicated variations with chemical composition of crystal structure and magnetic interactions. These concepts were first developed to account for cation ordering, lattice distortions, and magnetic interactions in spinel-type lattices[1]; their generality demands that they be valid for other crystal types. It is therefore significant that they apply so strikingly to this perovskite-type system.

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APPENDIX

Consider the following problem: assume that when a La^{3+} ion is replaced by a M^{2+} ion, two Mn^{3+} ions become Mn^{4+} and a neighboring La^{3+} becomes La^{2+} so as to minimize the Madelung energy of the configuration. Calculate the fraction of M^{2+} ions necessary to make half

the manganese ions Mn^{4+} if the M^{2+} ions replace lanthanum ions randomly and the replacement of a La^{2+} by M^{2+} causes no change in the valencies of the manganese ions. This problem has identical boundary conditions and is mathematically similar to the problem of calculating the fraction of randomly distributed Mn^{4+} ions which gives the largest number of Mn^{3+} ions with one, and only one, Mn^{4+} near neighbor.

Two Mn^{4+} ions are created by the first La^{3+} ion replaced by a M^{2+} ion. When the second lanthanum ion is replaced, the probability that it be a La^{2+} ion is $p_1 = 1/(N-1)$, and that it be a La^{3+} ion is $(1-p_1)$, where N is the total number of lanthanum ions present. When the third lanthanum ion is replaced, the probability that it be a La^{2+} ion is $p_2 = (2-p_1)/(N-2)$, and that it be a La^{3+} ion is $(1-p_2)$. When the $(n+1)$th lanthanum ion is replaced, the probability that it be a La^{2+} ion is $p_n = (n-p_{n-1})/(N-n)$, and that it be a La^{3+} ion is $(1-p_n)$. Half the manganese ions are Mn^{4+} when

$$2\left(n - \sum_n \frac{n - p_{n-1}}{N-n}\right) = \frac{N}{2}. \tag{1}$$

When N is large, the summation can be approximated by

$$\sum_n \frac{n}{N-n} \approx N \int_0^x \frac{x'dx'}{1-x'} = -N[x + \log(1-x)], \tag{2}$$

where $x = n/N$. Equation (1) reduces, therefore, to

$$2x = 0.25 - \log(1-x),$$
$$x = 0.31.$$

Symmetry Properties of the Energy Bands of the Zinc Blende Structure

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The symmetry properties of the one-electron energy bands of a crystal of the zinc blende structure are studied by means of group theory. This is done both with and without the inclusion of spin-orbit coupling. The character tables and compatability tables are obtained for the various irreducible representations of the space group T_d^2 associated with the zinc blende structure. The degeneracies and the gradients of the various possible energy bands are studied at lines and points of symmetry in the Brillouin zone. These results are compared with those for the equivalent energy bands in a crystal of the diamond structure.

I. INTRODUCTION

COMPOUNDS of the zinc blende structure are today assuming positions of increasing importance and interest in solid-state physics. The III–V compounds such as InSb are being intensively studied as semiconductors,[1] while II–VI compounds such as ZnS are used both as photoconductors and as phosphors.[2] There is

thus much interest in the nature of the one-electron energy bands in these compounds. Considerable information of a qualitative nature can be deduced about the energy-band maxima and minima in these compounds by means of a judicious combination of symmetry arguments, perturbation theory, and experimental information.[3] Here we propose to determine what can be said

[1] H. Welker, Z. Naturforsch. **7a**, 744 (1952); **8a**, 248 (1953).
[2] R. H. Bube, Phys. Rev. **83**, 393 (1951).

[3] F. Herman, J. Electronics (to be published); Phys. Rev. (to be published).
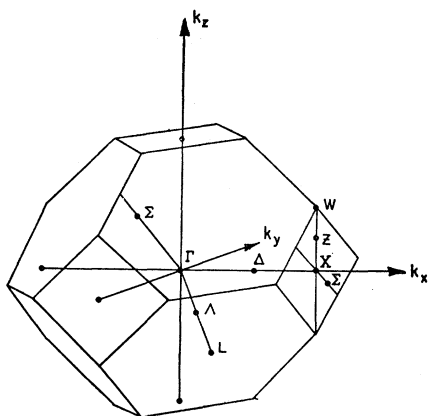
FIG. 1. Lines and points of symmetry in the Brillouin zone of the zinc blende structure

about the energy bands in these compounds on the basis of symmetry alone. In order to do this we will first construct the group-theoretic character tables associated with the zinc blende structure. These character tables are the basic quantities from which all symmetry properties will be deduced. As was first emphasized by Elliott[4] and by Dresselhaus, Kip, and Kittel,[5] the spin-orbit coupling energy,

$$(\hbar/4m^2c^2)[(\nabla V \times \mathbf{p}) \cdot \boldsymbol{\sigma}],\qquad(1)$$

may have a profound effect upon the one-electron energy levels in semiconductors. (Here V is the crystal potential, $\mathbf{p}$ the electron momentum operator, and $\boldsymbol{\sigma}$ the electron spin operator.) Therefore we will consider the symmetry problem first without and then with the inclusion of spin. Since the diamond structure may be considered to be a special case of the zinc blende structure (i.e., a IV–IV compound), we will compare some of the symmetry properties of the energy bands of the zinc blende structure with those of the diamond structure, character tables for the latter being available both with[6] and without[7] spin.

II. CHARACTER TABLES

The space groups of many of the simpler crystal structures are referred to as *point* space groups.[8] Every element of a point space group may be written as the product of an element of a translation group with an element of a point group, every element of the latter being either a rotation or the product of a rotation and an inversion. For example, the zinc blende structure has

the point space group $T_d{}^2$, associated with which are the face-centered cubic translation group and the tetrahedral point group T_d. Similarly, the face-centered cubic structure has the point space group $O_h{}^5$, associated with which are the face-centered cubic translation group and the full cubic point group O_h. (The space group for the diamond structure, $O_h{}^7$, however, is not a point space group.)

An electronic wave function without spin is a scalar function of position and always transforms into itself under a 360° rotation; with spin included, however, the wave function is a spinor and always transforms into the negative of itself under any 360° rotation.[9] Thus, if without spin a crystallographic point group contains n elements C_i, then with spin the point group will contain $2n$ elements, namely n elements C_i and n elements $\bar{C}_i$, where $\bar{C}_i$ is defined as

$$\bar{C}_i \equiv \bar{E} C_i,\qquad(2)$$

$\bar{E}$ being defined as some 360° rotation (E is the identity element). C_i and $\bar{C}_i$ are of course identical in their operation on a point in space. The crystallographic groups without and with spin are referred to as single and double groups, respectively.

Since in Schrödinger's equation the Hamiltonian operator H is such that H and H^* describe equivalent physical situations; i.e., H^* differs from H only by some unitary transformation U,

$$H^* = U^{-1}HU,\qquad(3)$$

it immediately follows[10] that any eigenfunction of H, namely $\Psi(\mathbf{r},t)$, is degenerate with $U\Psi^*(\mathbf{r}, -t)$, also an eigenfunction of H. Without electron spin in the Hamiltonian, $U=1$. With spin, $U=\sigma_y$, the y-component of the Pauli spin operator. This result is referred to as time-reversal symmetry in the Schrödinger equation[6,11,12] in addition to the crystallographic symmetries present. Time-reversal symmetry clearly leads to inversion symmetry of the energy bands in k-space. Since time-reversal symmetry is distinct from the symmetries associated with the space group, it will be necessary to consider the effects of the former after having constructed the character tables for the space group $T_d{}^2$.

The shape of the Brillouin zone in k-space associated with the zinc blende structure will be taken identical with that conventionally chosen for the diamond[7] and the face-centered cubic[13] structures, namely a truncated octahedron. Along with the lines and points of symmetry, it is shown in Fig. 1. It should be emphasized, however, that this choice of shape is not unique. In fact, the only parts of the surface of the Brillouin zone which are uniquely specified by symmetry are the lines Z

[4] Private communication to E. N. Adams, II. See E. N. Adams, II, Phys. Rev. 92, 1063 (1953), reference 7.

[5] Dresselhaus, Kip, and Kittel, Phys. Rev. 95, 568 (1954).

[6] R. J. Elliott, Phys. Rev. 96, 280 (1954). Elliott's character table for the extra representations of Λ and F is in error. The correct table is identical with Table III of the present paper; i.e., the character table for Λ and F is identical for the simple cubic, body-centered cubic, face-centered cubic, diamond, and zinc blende structures.

[7] C. Herring, J. Franklin Inst. 233, 525 (1942). Table XI of this reference is in error, but it is corrected in Table VIII of reference 6.

[8] W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc. New York, 1945), Chap. 2.

[9] See, for example, E. Feenberg and G. E. Pake, *Notes on the Quantum Theory of Angular Momentum* (Addison-Wesley Press, Cambridge, 1953), p. 28.

[10] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952), p. 525.

[11] E. Wigner, Gött. Nachr. p. 546 (1932).

[12] C. Herring, Phys. Rev. 52, 361 (1937).

[13] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936).

and the points L lying in the centers of the hexagonal faces. As far as the space group T_d^2 is concerned, L has no higher symmetry than that of Λ, so that L will not be mentioned in constructing the character tables. The additional symmetry of L arises from time-reversal.

Consider a given point space group. For a given wave vector $\mathbf{k}$ associated with some symmetry point in k-space, we find those operations of the point group associated with the space group which transform $\mathbf{k}$ into itself plus some reciprocal-lattice vector. Such a set of operations forms a group called the group of the wave vector $\mathbf{k}$. There will be a distinct wave-vector group for each type of symmetry line and point in the Brillouin zone. All the wave-vector groups are subgroups of the point group associated with the space group. We now determine the members of the wave-vector group for zinc blende for each type of symmetry point in the Brillouin zone and compare each of these groups with the corresponding wave-vector group for the face-centered cubic structure as given in reference 13 (without spin) and reference 6 (with spin). (We use the terminology of reference 13 to denote the group operations and the lines and points of symmetry.) For Λ, the wave-vector groups for zinc blende and fcc are identical, and thus so are the character tables (note comment of reference 6). For both Γ and X. the wave-vector group for fcc is the direct product of the corresponding wave-vector group for zinc blende and the group of order two, $\mathfrak{C}_2$, whose elements are E, the identity element, and J, the inversion element.[14] Group theory states that, con-

TABLE I. Character table for the representations of the single group of Γ.

24	Γ	Γ_1	Γ_2	Γ_{12}	Γ_{15}	Γ_{25}
1	E	1	1	2	3	3
3	C_4^2	1	1	2	-1	-1
8	C_3	1	1	-1	0	0
6	JC_4	1	-1	0	-1	1
6	JC_2	1	-1	0	1	-1

TABLE II. Character table for the representations of the single group of Δ. (The two distinct operations JC_2 are those about the two twofold axes perpendicular to Δ.) Δ_3 and Δ_4 stick together.

4	Δ	Δ_1	Δ_2	Δ_3	Δ_4
1	E	1	1	1	1
1	JC_2	1	-1	1	-1
1	JC_2	1	-1	-1	1
1	$C_4^2{}_{\parallel}$	1	1	-1	-1

TABLE III. Character table for the representations of the single group of Λ.

6	Λ	Λ_1	Λ_2	Λ_3
1	E	1	1	2
2	C_3	1	1	-1
3	JC_2	1	-1	0

[14] Consider a group $\mathfrak{A}$ with elements a_i and a group $\mathfrak{B}$ with elements b_j, where $a_i b_j = b_j a_i$. The direct product of groups $\mathfrak{A}$ and $\mathfrak{B}$ is a group $\mathfrak{C} = \mathfrak{A} \times \mathfrak{B}$ whose elements are $c_{ij} = a_i b_j$.

TABLE IV. Character table for the representations of the single groups of Σ and Z.

2	Σ	Z	Σ_1	Σ_2
1	E	E	1	1
1	JC_2	$C_4^2{}_{\perp}$	1	-1

TABLE V. Character table for the representations of the single group of X.

8	X	X_1	X_2	X_3	X_4	X_5
1	E	1	1	1	1	2
2	$C_4^2{}_{\perp}$	1	1	-1	-1	0
1	$C_4^2{}_{\parallel}$	1	1	1	1	-2
2	$JC_4{}_{\parallel}$	1	-1	-1	1	0
2	JC_2	1	-1	1	-1	0

TABLE VI. Character table for the representations of the single group of W. (The two distinct operations JC_4 are those about the fourfold axis parallel to the face diagonal containing W.) W_3 and W_4 are degenerate by time-reversal symmetry.

4	W	W_1	W_2	W_3	W_4
1	E	1	1	1	1
1	JC_4	1	-1	i	$-i$
1	JC_4	1	-1	$-i$	i
1	C_4^2	1	1	-1	-1

sidered as a matrix,[15] the character table appropriate to a direct-product group is itself the direct product[16] of the matrices representing the character tables of the groups occurring as factors of the direct-product group.[17] With the aid of the character table of the group $\mathfrak{C}_2$ (it is equivalent to Table IV), it is a simple matter to obtain the character tables for zinc blende for the points Γ and X from the corresponding character tables for fcc. Considering the Σ and Z lines in zinc blende, it is apparent that without spin these wave-vector groups each contain only two elements and are thus both simply isomorphic with the group $\mathfrak{C}_2$. Including spin, it is evident that these two groups are simply isomorphic with the cyclic group of order four. Thus for each group the characters are the appropriate powers of a fourth root of unity.[18] Turning to the point W, without spin the wave-vector group is also the fourth-order cyclic group, the elements of the group being various powers of JC_4, an inversion combined with a 90° rotation about the fourfold axis parallel to the face diagonal containing W.

[15] A character table may be considered a square matrix whose rows designate the classes of elements and whose columns designate the irreducible representations.

[16] The direct product of an $m \times m$ matrix having elements α_{ij} and an $n \times n$ matrix having elements $\beta_{i'j'}$ is an $mn \times mn$ matrix having elements $\alpha_{ij}\beta_{i'j'}$, i and i' designating the row and j and j' the column.

[17] F. D. Murnaghan, *The Theory of Group Representations* (Johns Hopkins Press, Baltimore, 1938), p. 101.

[18] The cyclic group of order n contains the elements C, C^2, C^3, $\cdots C^n = E$. Since any two elements commute, each element forms a class by itself. Since there are n classes, there are n representations, each necessarily one-dimensional. A one-dimensional representation and its character being identical, the characters must transform as do their corresponding group elements and thus must be appropriate powers of an nth root of unity.

TABLE VII. Character table for the extra representations of the double group of Γ.

48	Γ	Γ_6	Γ_7	Γ_8
1	E	2	2	4
1	$\bar{E}$	-2	-2	-4
6	$C_4{}^2, \bar{C}_4{}^2$	0	0	0
8	C_3	1	1	-1
8	$\bar{C}_3$	-1	-1	1
6	JC_4	$\sqrt{2}$	$-\sqrt{2}$	0
6	$J\bar{C}_4$	$-\sqrt{2}$	$\sqrt{2}$	0
12	$JC_2, J\bar{C}_2$	0	0	0

TABLE VIII. Character table for the extra representation of the double group of Δ.

8	Δ	Δ_5
1	E	2
1	$\bar{E}$	-2
2	$JC_2, J\bar{C}_2$	0
2	$JC_2, J\bar{C}_2$	0
2	$C_4{}^2{}_{||}, \bar{C}_4{}^2{}_{||}$	0

TABLE IX. Character table for the extra representations of the double group of Λ, Λ_4, and Λ_5 are degenerate by time-reversal symmetry.

12	Λ	Λ_4	Λ_5	Λ_6
1	E	1	1	2
1	$\bar{E}$	-1	-1	-2
2	C_3	-1	-1	1
2	$\bar{C}_3$	1	1	-1
3	JC_2	i	$-i$	0
3	$J\bar{C}_2$	$-i$	i	0

Similarly, with spin the wave-vector group is the eighth-order cyclic group, so that the characters are the appropriate powers of an eighth root of unity. For the fourfold axis Δ, without spin the wave-vector group contains the identity element E, the two commuting elements JC_2 (representing reflections in the planes perpendicular to the twofold axes which are in turn perpendicular to Δ), and the element $C_4{}^2{}_{||}$ (representing a 180° rotation about Δ) which is the product of the two reflections. Thus the group may be considered to be the direct product of two second-order groups $\mathfrak{C}_2$, and the character table follows immediately. With spin the wave-vector group for Δ can be seen to be simply isomorphic with the group for X without spin, with the result that the two character tables are equivalent.

In this simple fashion we have obtained the character tables for the zinc blende structure for both the single and the double groups. The single groups without spin are listed in Tables I–VI. A perusal of our results demonstrates a rule generally valid[19] that the irreducible representations of the single group occur unchanged in the double group with the elements C_i and $\bar{C}_i$ having the same character. For this reason, we do not bother to list these representations again in the double groups, but restrict ourselves to listing the additional or *extra* representations, which are given in Tables VII–XII. In

[19] W. Opechowski, Physica **7**, 552 (1940).

contrast with the other representations, the extra representations always occur with the elements C_i and $\bar{C}_i$ having characters of opposite sign. (Thus whenever C_i and $\bar{C}_i$ occur in the same class, the corresponding characters of the extra representations always vanish.)

III. RESULTS

As we move continuously in k-space from a point of higher symmetry to a point of lower symmetry, we wish to know how the various irreducible representations associated with the former point transform into those associated with the latter point. To do this we construct what are known as compatability tables.[13] We express the characters of a representation for the higher-symmetry point in terms of a sum of corresponding characters of lower-symmetry representations, this to be done simultaneously for each group operation common to the two points. These lower-symmetry representations are what combine at the higher-symmetry point to form the higher-symmetry representation. The compatability tables for the single groups without spin are given in Table XIII, and those for the double groups with spin (extra representations) are given in Table XIV.

Physically, the zinc blende structure may be considered to be the result of a deformation upon either the face-centered cubic structure, $O_h{}^5$, or the diamond structure $O_h{}^7$. Thus we may construct a second type of

TABLE X. Character table for the extra representations of the double groups of Σ and Z. Σ_3 and Σ_4, Z_3 and Z_4, are degenerate by time-reversal symmetry.

4	Σ	Z	Σ_3	Σ_4
1	E	E	1	1
1	$\bar{E}$	$\bar{E}$	-1	-1
1	JC_2	$C_4{}^2{}_\perp$	i	$-i$
1	$J\bar{C}_2$	$\bar{C}_4{}^2{}_\perp$	$-i$	i

TABLE XI. Character table for the extra representations of the double group of X.

16	X	X_6	X_7
1	E	2	2
1	$\bar{E}$	-2	-2
4	$C_4{}^2{}_\perp, \bar{C}_4{}^2{}_\perp$	0	0
2	$C_4{}^2{}_{||}, \bar{C}_4{}^2{}_{||}$	0	0
2	$JC_4{}_{||}$	$\sqrt{2}$	$-\sqrt{2}$
2	$J\bar{C}_4{}_{||}$	$-\sqrt{2}$	$\sqrt{2}$
4	$JC_2, J\bar{C}_2$	0	0

TABLE XII. Character table for the extra representations of the double group of W. W_5 is degenerate with W_7 and W_6 is degenerate with W_8 by time-reversal symmetry. $\epsilon = (1+i)/\sqrt{2}$.

8	W	W_5	W_6	W_7	W_8
1	E	1	1	1	1
1	$\bar{E}$	-1	-1	-1	-1
1	JC_4	ϵ	$-\epsilon$	ϵ^*	$-\epsilon^*$
1	$J\bar{C}_4$	$-\epsilon$	ϵ	$-\epsilon^*$	ϵ^*
1	JC_4	ϵ^*	$-\epsilon^*$	ϵ	$-\epsilon$
1	$J\bar{C}_4$	$-\epsilon^*$	ϵ^*	$-\epsilon$	ϵ
1	$C_4{}^2$	i	i	$-i$	$-i$
1	$\bar{C}_4{}^2$	$-i$	$-i$	i	i

TABLE XIII. Compatability tables for the representations of the single groups connecting symmetry points with symmetry axes.

Γ	Δ	Λ	Σ
Γ_1	Δ_1	Λ_1	Σ_1
Γ_2	Δ_2	Λ_2	Σ_2
Γ_{12}	$\Delta_1+\Delta_2$	Λ_3	$\Sigma_1+\Sigma_2$
Γ_{15}	$\Delta_1+\Delta_3+\Delta_4$	$\Lambda_1+\Lambda_3$	$2\Sigma_1+\Sigma_2$
Γ_{25}	$\Delta_2+\Delta_3+\Delta_4$	$\Lambda_2+\Lambda_3$	$\Sigma_1+2\Sigma_2$

X	Δ	Σ	Z
X_1	Δ_1	Σ_1	Z_1
X_2	Δ_2	Σ_2	Z_1
X_3	Δ_1	Σ_1	Z_2
X_4	Δ_2	Σ_2	Z_2
X_5	$\Delta_3+\Delta_4$	$\Sigma_1+\Sigma_2$	Z_1+Z_2

W	Z
W_1	Z_1
W_2	Z_1
W_3	Z_2
W_4	Z_2

TABLE XIV. Compatability tables for the extra representations of the double groups connecting symmetry points with symmetry axes.

Γ	Δ	Λ	Σ
Γ_6	Δ_5	Λ_6	$\Sigma_3+\Sigma_4$
Γ_7	Δ_5	Λ_6	$\Sigma_3+\Sigma_4$
Γ_8	$2\Delta_5$	$\Lambda_4+\Lambda_5+\Lambda_6$	$2\Sigma_3+2\Sigma_4$

X	Δ	Σ	Z
X_6	Δ_5	$\Sigma_3+\Sigma_4$	Z_3+Z_4
X_7	Δ_5	$\Sigma_3+\Sigma_4$	Z_3+Z_4

W	Z
W_5	Z_3
W_6	Z_3
W_7	Z_4
W_8	Z_4

compatability table between $T_d{}^2$ and $O_h{}^5$ and between $T_d{}^2$ and $O_h{}^7$, showing how the various irreducible representations for $O_h{}^5$ and $O_h{}^7$ are transformed by the deformations which convert these structures into $T_d{}^2$. Using the same technique described in the previous paragraph, we obtain Tables XV and XVI. Such tables are particularly useful in looking at some zinc blende structure as a perturbation upon some similar diamond structure,[3] e.g., GaAs as a perturbation upon Ge.

A third type of compatibility table is needed to show how the various irreducible representations for zinc blende without spin are transformed upon the introduction of spin. Such information is given in Table XVII, which demonstrates the general rule that only the *extra* irreducible representations occur.[6] Table XVII is obtained in the following fashion. If we take the point group T_d and replace the elements JC_4 (90° rotation about a fourfold axis followed by an inversion) and JC_2 (180° rotation about a twofold axis followed by an inversion) by C_4 and C_2 respectively, we obtain the point group O, which can be seen to be simply isomorphic with T_d. Since O is a subgroup of the rotation group δ_3, it follows that a conventional compatability table can be

set up connecting the representations of δ_3 with those of T_d. A wave function of spin alone belongs to the $D_{\frac{1}{2}}$ representation of δ_3. Since the explicit form of the $D_{\frac{1}{2}}$ representation matrices is available in the literature[6,19] the characters can be calculated, whence it is found that $D_{\frac{1}{2}}$ corresponds to the Γ_6 representation of the T_d point group. An eigenfunction of our Hamiltonian containing spin for the zinc blende structure will be a sum of products of a function of spin (belonging to the $D_{\frac{1}{2}}$ representation) and a function of position (belonging to some representation Ξ_i of the single space group $T_d{}^2$). Thus this eigenfunction will belong to one of the irreducible representations contained in the direct product $\Xi_i \times \Gamma_6$. Table XVII is now obtained by making use of the fact that a character of the direct product of two representations, which is the product of the corresponding characters of the two representations, can be written as the sum of the corresponding characters of all the irreducible representations composing the direct product.

We are now in a position to study the nature of the energy bands in zinc blende (as imposed by symmetry). First we consider the possibility of the sticking together of two bands associated with distinct representations; i.e., two wave functions of a given **k** being degenerate although belonging to two distinct representations. An operation of the class $JC_{4\parallel}$ (rotation by 90° about the axis Δ followed by an inversion) followed by the time-reversal symmetry operation (replacing **k** by $-$**k**) will convert a wave function belonging to Δ_3 into one

TABLE XV. Compatability tables for the representations of the single groups connecting the zinc blende $(T_d{}^2)$ with the face-centered-cubic $(O_h{}^5)$ and the diamond $(O_h{}^7)$ structures.

$T_d{}^2$	$O_h{}^5$	$T_d{}^2$	$O_h{}^7$
Γ_1	Γ_1 or $\Gamma_{2'}$	Γ_1	Γ_1 or $\Gamma_{2'}$
Γ_2	Γ_2 or $\Gamma_{1'}$	Γ_2	Γ_2 or $\Gamma_{1'}$
Γ_{12}	Γ_{12} or $\Gamma_{12'}$	Γ_{12}	Γ_{12} or $\Gamma_{12'}$
Γ_{15}	Γ_{15} or $\Gamma_{25'}$	Γ_{15}	Γ_{15} or $\Gamma_{25'}$
Γ_{25}	Γ_{25} or $\Gamma_{15'}$	Γ_{25}	Γ_{25} or $\Gamma_{15'}$
Δ_1	Δ_1 or $\Delta_{2'}$	Δ_1	Δ_1 or $\Delta_{2'}$
Δ_2	Δ_2 or $\Delta_{1'}$	Δ_2	Δ_2 or $\Delta_{1'}$
Δ_3 $\}$ Δ_4	Δ_5	Δ_3 $\}$ Δ_4	Δ_5
Λ_1	Λ_1	Λ_1	Λ_1
Λ_2	Λ_2	Λ_2	Λ_2
Λ_3	Λ_3	Λ_3	Λ_3
Σ_1	Σ_1 or Σ_3	Σ_1	Σ_1 or Σ_3
Σ_2	Σ_2 or Σ_4	Σ_2	Σ_2 or Σ_4
Z_1	Z_1 or Z_2	Z_1 $\}$ Z_2	Z_1
Z_2	Z_3 or Z_4		
X_1	X_1 or $X_{2'}$	X_1 $\}$ X_3	X_1
X_2	X_2 or $X_{1'}$		
X_3	X_3 or $X_{4'}$	X_2 $\}$ X_4	X_2
X_4	X_4 or $X_{3'}$		
X_5	X_5 or $X_{5'}$	X_5	X_3 or X_4
W_1	W_1 or W_2	W_1 $\}$ W_3	W_1
W_2	$W_{1'}$ or $W_{2'}$		
W_3 $\}$ W_4	W_3	W_2 $\}$ W_4	W_2

TABLE XVI. Compatability tables for the extra representations of the double groups connecting the zinc blende (T_d^2) with the face-centered cubic (O_h^5) and the diamond (O_h^7) structures.

T_d^2	O_h^5	T_d^2	O_h^7
Γ_6	Γ_6^+ or Γ_7^-	Γ_6	Γ_6^+ or Γ_7^-
Γ_7	Γ_6^- or Γ_7^+	Γ_7	Γ_6^- or Γ_7^+
Γ_8	Γ_8^+ or Γ_8^-	Γ_8	Γ_8^+ or Γ_8^-
Δ_5	Δ_6 or Δ_7	Δ_5	Δ_6 or Δ_7
Λ_4	Λ_4	Λ_4	Λ_4
Λ_5	Λ_5	Λ_5	Λ_5
Λ_6	Λ_6	Λ_6	Λ_6
$\left.\begin{array}{l}\Sigma_3\\\Sigma_4\end{array}\right\}$	Σ_5	$\left.\begin{array}{l}\Sigma_3\\\Sigma_4\end{array}\right\}$	Σ_5
$\left.\begin{array}{l}Z_3\\Z_4\end{array}\right\}$	Z_5	$\left.\begin{array}{l}Z_3\\Z_4\end{array}\right\}$	Z_5
X_6	X_6^+ or X_7^-	$\left.\begin{array}{l}X_6\\X_7\end{array}\right\}$	X_5
X_7	X_6^- or X_7^+		
$\left.\begin{array}{l}W_5\\W_7\end{array}\right\}$	W_6	W_5	$\left.\begin{array}{l}W_3 \text{ or } W_5 \text{ or}\\W_4 \text{ or } W_6 \text{ or}\end{array}\right\}W_7$
$\left.\begin{array}{l}W_6\\W_8\end{array}\right\}$	W_7	W_6	
		W_7	$\left.\begin{array}{l}W_3 \text{ or } W_5 \text{ or}\\W_4 \text{ or } W_6 \text{ or}\end{array}\right\}W_7$
		W_8	

belonging to Δ_4, while leaving $\mathbf{k}$ and the Hamiltonian invariant. Thus Δ_3 and Δ_4 stick together. In a similar fashion, at the point L the time-reversal symmetry operation will convert a wave function belonging to Λ_4 into Λ_5, while leaving $\mathbf{k}$ and the Hamiltonian invariant. Thus Λ_4 and Λ_5 stick together at the point L. These are the only cases of bands sticking together as a result of time-reversal symmetry. Since, however, the characters belonging to the representation Z_3 are complex conjugates of those belonging to Z_4, it follows from time-reversal symmetry that for every wave function of a given wave vector $\mathbf{k}$ belonging to Z_3 there is a degenerate wave function of $-\mathbf{k}$ belonging to Z_4. Identical arguments hold for Λ_4 and Λ_5, for Σ_3 and Σ_4, for W_3 and W_4, W_5 and W_7, and W_6 and W_8, respectively.[20]

As was emphasized by Elliott,[21] at a point of no special symmetry in k-space, the extra representations are always doubly degenerate in crystals possessing a center of inversion, such as diamond. Because of the lack of inversion symmetry, this is not the case in zinc blende. We wish to investigate whether or not, on the basis of symmetry, the gradient in k-space of a given energy band will vanish in a given direction at a given point in k-space. Since $\nabla_k E(\mathbf{k})$ is proportional to the expectation value of momentum, it is necessary to investigate whether or not the matrix elements of $(\hbar/i)\nabla$ vanish, these matrix elements being taken with respect to the wave functions belonging to a particular irreducible representation of the wave-vector group associated with the given point in k-space. For the component of the gradient along a direction specified by the unit vector $\mathbf{u}$,

we need to consider matrix elements of $(\hbar/i)\mathbf{u}\cdot\nabla$, these matrix elements being integrals over ordinary space.[22] The integrands of these integrals transform into one another under those particular operations associated with the given wave vector group which transform $\mathbf{u}\cdot\nabla$ into either plus or minus itself (the operation acting on ∇ but not on $\mathbf{u}$). Such operations form a group which we shall call the gradient wave-vector group. If we knew the character tables of the gradient wave-vector groups, it would be an easy matter to decide whether or not a given matrix element vanishes. Thus we would resolve the representation to which the integrand belongs (the direct product of the three representations corresponding to the two wave functions in the integrand and to $\mathbf{u}\cdot\nabla$, respectively) into a sum of irreducible representations of the gradient wave vector group, in exactly the same manner used to obtain Table XVII. We now make use of the fact that the integral will vanish unless the sum of irreducible representations contains the totally symmetric representation (that representation all of whose characters are unity).[23,24] We actually have the character tables of the gradient wave-vector groups, since every gradient wave-vector group is simply isomorphic with some particular wave-vector group.[25]

TABLE XVII. Compatability table connecting the representations of the single groups with the extra representations of the double groups.

Ξ_i	$\Xi_i\times\Gamma_6$	Ξ_i	$\Xi_i\times\Gamma_6$
Γ_1	Γ_6	Σ_1	$\Sigma_3+\Sigma_4$
Γ_2	Γ_7	Σ_2	$\Sigma_3+\Sigma_4$
Γ_{12}	Γ_8	Z_1	Z_3+Z_4
Γ_{15}	$\Gamma_7+\Gamma_8$	Z_2	Z_3+Z_4
Γ_{25}	$\Gamma_6+\Gamma_8$		
Δ_1	Δ_5	X_1	X_6
Δ_2	Δ_5	X_2	X_7
Δ_3	Δ_5	X_3	X_7
Δ_4	Δ_5	X_4	X_6
		X_5	X_6+X_7
Λ_1	Λ_6		
Λ_2	Λ_6	W_1	W_5+W_7
Λ_3	$\Lambda_4+\Lambda_5+\Lambda_6$	W_2	W_6+W_8
		W_3	W_5+W_8
		W_4	W_6+W_7

[20] The writer is indebted to G. Dresselhaus, who has independently studied the symmetry properties of the zinc blende structure, for pointing out errors in the writer's original analysis of the effect of time-reversal symmetry on the points Λ and Σ for the double groups.

[21] R. J. Elliott, Phys. Rev. 96, 266 (1954).

[22] For the spin case, ∇ should be replaced by $[\nabla+(i/4mc^2)(\boldsymbol{\sigma}\nabla\times V]$. The latter, however, has the same transformation properties as ∇ and need not be considered further.

[23] See, for example, Eyring, Walter, and Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944), p. 187.

[24] In some cases where the above analysis does not indicate a vanishing gradient, it is evident that the gradient must vanish in order to maintain time-reversal symmetry.

[25] The gradient wave-vector groups at Γ for $\mathbf{u}$ pointing along Δ, Λ, and Σ are simply isomorphic with the wave-vector groups at X, Λ, and Δ, respectively. The gradient wave-vector groups at X for $\mathbf{u}$ pointing along Δ, Σ, and Z are simply isomorphic with the wave-vector groups at X, Δ, and Δ, respectively. The gradient wave-vector groups at W for $\mathbf{u}$ pointing along Z and along either of the two (100) directions perpendicular to Z are simply isomorphic with the wave-vector groups at W and Σ, respectively. The gradient wave-vector groups at Δ for $\mathbf{u}$ pointing along a perpendicular (100) direction and along a perpendicular (110) direction (both perpendicular to Δ) are simply isomorphic with the wave-vector groups at Σ and Δ, respectively. The gradient wave-vector groups at Λ, Σ, and Z are all simply isomorphic with the wave-vector group at Σ.

Finally, we wish to point out two facts which are useful in any study of energy bands. The first is that the complete set of energy bands must have the full symmetry of the Brillouin zone. The second is that, as we move along a continuous curve (with continuous derivatives) in k-space, it is always possible to trace out a continuous curve (with continuous derivatives) of allowed energy *versus* k.

With the aid of the considerations of the previous paragraphs it is now possible to deduce the nature of the energy bands in the vicinity of a symmetry point. First we consider the single groups without spin. For this case the energy bands are identical in their symmetry properties with those of the diamond structure everywhere except along the symmetry axes Σ and Z. As in diamond, Γ is a point of zero slope in the directions of the three symmetry axes Δ, Λ, and Σ; L is a point of zero slope in the direction of Λ; Δ is a point of zero slope along the (100) and (110) directions perpendicular to the given Δ axis; and Λ may be a point of either zero slope or finite slope in directions perpendicular to the given Λ axis (Λ_1 and Λ_2 have zero slope, Λ_3 has finite slope). Although Σ is nondegenerate as in diamond, it differs from diamond in that it is a point of finite slope along the (100) direction perpendicular to the given Σ axis (although it is a point of zero slope along the (110) direction perpendicular to the given Σ axis). If we consider the square-face diagonals, unlike diamond X is always a point of zero slope along the three symmetry axes Δ, Σ, and Z, while Z and W are nondegenerate, W being a point of zero slope in any direction and Z being a point of zero slope in directions normal to the given Z-axis.

We now consider the double groups with spin. For this case the energy bands of the zinc blende structure are considerably different from those of the diamond structure. The types of possible E *versus* k curves in the neighborhoods of symmetry points are shown in Fig. 2. Γ_6 and Γ_7 are points of zero slope along Δ and Λ but finite slope along Σ, while Γ_8 may be a point of finite slope in any direction (although Λ_6 will approach Γ_8 with zero slope), as has been suggested by Kittel and Dresselhaus.[26] Λ_4 and Λ_5 approach L with finite slope while Λ_6 approaches L with zero slope. X is a point of zero slope along Δ and finite slope along Σ and Z. W is a point of zero slope in any direction. Δ is a point of finite slope in directions normal to the given Δ axis. Λ may be a point of either zero slope or finite slope in directions perpendicular to the given Λ axis (Λ_4 and Λ_5 have zero slope, Λ_6 has finite slope). At Σ or Z the slopes in directions perpendicular to their respective axes are similar to those for Σ and Z in the absence of spin. Unlike diamond, at many points in k-space a nondegenerate band may occur. We see that the only points of special symmetry at which an energy band minimum or maximum can occur on the basis of symmetry alone are the points W. A minimum or max-
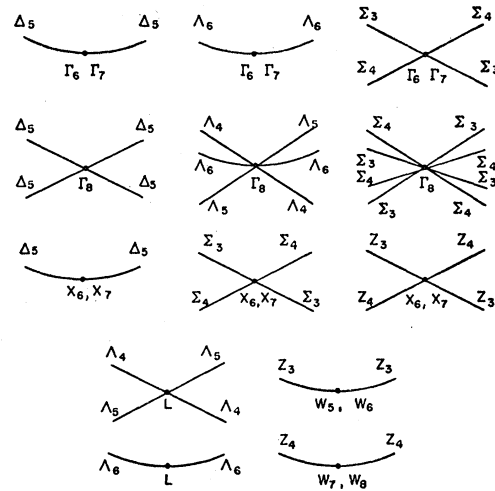
[26] C. Kittel (private communication).

FIG. 2. Nature of possible E *versus* k curves in the neighborhood of symmetry points.

imum *may* occur somewhere along Λ or Z, but none will occur along Δ or Σ, or at the points Γ, X, or L.

In conclusion, we might point out that if we look at the zinc blende structure as a perturbation on the diamond structure,[3] then the difference between a given energy level of the unperturbed diamond structure and the corresponding energy level of the perturbed zinc blende structure will vanish (to the accuracy of first-order perturbation theory) everywhere except on the square-face diagonals in the case of no spin, but will vanish only along the axis Δ (including Γ but excluding X) in the case of spin. To prove this, we first note that the perturbation potential which converts a diamond structure into a zinc blende structure will have odd parity with respect to an inversion about a point midway between two adjacent atoms. By combining degenerate unperturbed diamond-structure wave functions associated with different values of k, we can always form new unperturbed wave functions which have either even or odd parity with respect to inversion about such a point midway between two adjacent atoms. It now follows that all diagonal matrix elements of the perturbation potential with respect to these new unperturbed wave functions will vanish, and thus the sum of diagonal matrix elements over a degenerate set of unperturbed wave functions, i.e., the trace, will vanish. This means that first-order perturbation theory may split a degeneracy but will not affect its "center-of-gravity" (mean energy). But Tables XV and XVI show that, in the case of no spin, degeneracies are split only along the square-face diagonals, whereas, when spin is present, degeneracies are split everywhere except along the axis Δ (including Γ but excluding X). This completes the proof.

IV. ACKNOWLEDGMENTS