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Symmetry of Wurtzite

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The symmetry analysis of wurtzite, performed originally by Dresselhaus at the origin of the Brillouin zone, is extended. A method is employed at the zone boundaries which is considerably simpler than the standard procedure. Optical selection rules for band-to-band transitions in the neighborhood of $\mathbf{k}=0$ are re-examined. It is found that light polarized perpendicular to the c axis should be absorbed more strongly than light polarized along the c axis, independently of the symmetry types of the initial and final states, unless they have the same symmetry, which is unlikely. This result is in agreement with experiment for CdS and ZnS.

I. INTRODUCTION

Since the fundamental work of Bethe[1] and of Seitz,[2,3] a number of authors[4–11] have contributed to the group-theoretical classification of the symmetry properties of various crystalline structures. Recent experiments on optical absorption[12–14] and cyclotron resonance[15] in structures of the wurtzite type indicate a need for a better understanding of this species. Dresselhaus[16] has reported on the results of an analysis at the origin of the Brillouin zone in connection with his theory of the dichroic optical absorption exhibited by crystals having this symmetry. In a recent review article by Herman,[17] Parmenter is reported to have extended this work to other points in the zone. Unfortunately, there is an error in the paper by Dresselhaus which, although minor, leads to nontrivial consequences of a physical nature. Moreover, since in the present analysis, a method is employed which obviates explicit reduction of the full factor group,[18] $G^{\mathbf{k}}/T^{\mathbf{k}}$ at the zone boundaries, despite the presence of fractional translations in the space group, a brief note on this subject may be worthwhile.

Let G be the space group consisting of lattice operations which, in the notation of Seitz,[2] may be expressed in the form, $(\alpha|\mathbf{v}_\alpha+\mathbf{t})$, where α is a real orthogonal matrix, $\mathbf{v}_\alpha$ is a fractional lattice translation, and $\mathbf{t}$ is a translation in the Bravais lattice. For brevity we shall sometimes write $\mathbf{a}$ in place of $\mathbf{v}_\alpha+\mathbf{t}$. Let T denote the invariant subgroup of translations, $(\epsilon|\mathbf{t})$ of the hexagonal lattice. A simplification can be achieved in the case of the wurtzite structure if we select our origin of coordinates as pictured in Fig. 1 rather than at an atomic site as was done by Herring[5] in connection with the monatomic hexagonal lattice. From Fig. 1 we may enumerate the operations in the factor group, G/T as follows: There are six operations of the form $(\delta^n|\mathbf{v}_n)$, where δ is a rotation by $2\pi/6$ about the c axis, n is an integer which takes on values from zero through five, and $\mathbf{v}_n$ is zero if n is even and is equal to $\mathbf{t}_3/2$ if n is odd. Here, $\mathbf{t}_3$ is the basic lattice vector parallel to the c axis. In addition, there are six operations of the form $(\delta^n|\mathbf{v}_n)(\sigma|0)$, where σ is a reflection in the plane $x=0$. When considering the group of the wave vector, $G^{\mathbf{k}}$ for values of $\mathbf{k}$ lying in the interior of the zone, this choice of origin holds no special advantage; at the zone boundaries, however, it will be shown to result in a considerable simplification of the problem. At the origin of the zone we shall follow the standard procedure of considering the factor group $G^{\mathbf{k}}/T^{\mathbf{k}}$, where $T^{\mathbf{k}}$ is the invariant subgroup of translations $(\epsilon|\mathbf{t})$ which satisfy the condition $\exp(-i\mathbf{k}\cdot\mathbf{t})=1$.

As is well known, at the origin $G^{\mathbf{k}}/T^{\mathbf{k}}$ equals G/T, which is isomorphic to the point group[19] C_{6v}, consisting of elements δ^n and $\delta^n\sigma$. Furthermore, C_{6v} is isomorphic to the point group D_6 which contains elements of the form δ^n and $\delta^n\rho$, where ρ is a rotation by π about the x axis (Fig. 1). That is, $\sigma=J\rho$, where J is the inversion element. Although the chain of isomorphisms allows one to derive the character table of the double group[8,9] of G/T by considering the double group of D_6, it is incorrect to assume that the components of the mo-

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[16] G. Dresselhaus, Phys. Rev. **105**, 135 (1957); contains references to earlier experimental work.

[17] F. Herman, Revs. Modern Phys. **30**, 102 (1958). Table I in this reference contains an extensive list of structures for which symmetry analyses have been performed. The writer was unaware of Dr. Parmenter's unpublished work during the period in which the present analysis was performed.

[18] This group is defined in a subsequent paragraph. See also reference 5.

[19] Character tables for all the point groups, including the double groups, are presented in a review article by G. F. Koster, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 173.

mentum operator $\mathbf{p}$ transform according to representations[20] of D_6. Physically, the operators of the double group are those which commute with the spin-orbit coupling term,[9] $\boldsymbol{\sigma}\cdot(\nabla V\times\mathbf{p})$, in the Hamiltonian, where $\boldsymbol{\sigma}$ is the Pauli vector and V is the periodic potential. For wurtzite, these operators have the explicit form

$$(\delta^n|\mathbf{v}_n)[\pm u(\delta^n)] \quad\text{and}\quad (\delta^n\sigma|\mathbf{v}_n)[\pm u(\delta^n\rho)], \tag{1}$$

where u is the two-dimensional spin operator.[21] The assignment of Γ_2 to the z component of $\mathbf{p}$ in reference 16 would imply that the second set of operators in expression (1) are of the form

$$(\delta^n\rho|\mathbf{v}_n)[\pm u(\delta^n\rho)]. \tag{2}$$

Operations of this type are not in the double group of G/T, however, since $(\delta^n\rho|\mathbf{v}_n)$ is not a covering operation of the crystal. In fact, p_z transforms according to the identity representation, Γ_1. This observation leads to different conclusions with regard to matrix elements of $\boldsymbol{\varepsilon}\cdot\mathbf{p}$, which are relevant in determining optical selection rules, and of $\mathbf{k}\cdot\mathbf{p}$, which are useful in examining $\text{grad}_{\mathbf{k}}E(\mathbf{k})$ at various points in the zone. Here, $\boldsymbol{\varepsilon}$ is the polarization vector of the exciting light in optical experiments and $E(\mathbf{k})$ is the band energy.

For example, if one assumes Dresselhaus' optical model,[16] subsequent analysis shows that light polarized perpendicular to the c axis should be more strongly absorbed than light polarized parallel to the c axis, *independently* of the symmetry types of the conduction and valence bands involved in the optical process. The one exception to this rule occurs if the symmetry types are the same for both the initial and final states, an unlikely event at $\mathbf{k}=0$. This general qualitative prediction, which cannot be made if p_z is assumed to transform according to Γ_2, is in agreement with the experimental observations of Dutton[13] for CdS and of Piper, Marple, and Johnson[14] and Keller and Pettit[22] for ZnS. The correction does not allow one to explain the exponential frequency dependence of the absorption coefficient in CdS, however. In all likelihood a different model, perhaps involving excitons, will be necessary to bring about agreement between theory and experiment. Nevertheless, it is not unreasonable to assume that in some approximation, the argument presented is still valid, since the argument is probably more general than the model to which it has been applied. A derivation of the selection rule and further comparison with experiment is contained in Sec. III.

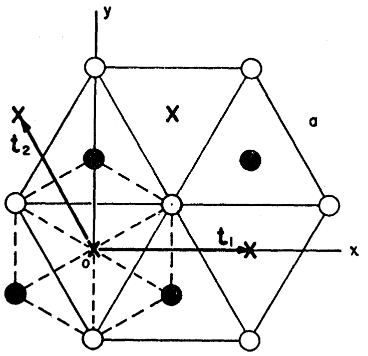

FIG. 1. Projection of the wurtzite structure on a basal plane normal to the c axis. The open circles represent the A-lattice and the closed circles the B-lattice in the familiar $ABAB$ stacking sequence of close packed hexagonal structures. The crosses designate the vacant C-lattice. The origin of coordinates is chosen along a line connecting C-lattice sites in the z direction (i.e., parallel to the c axis) at a point midway between a plane of close packing in the A-lattice and the corresponding adjacent plane in the B-lattice. The operations in the factor group G/T are pictured most easily if attention is focussed on the smaller hexagon, shown dashed. Any operation in C_{6v} which transforms an open circle into a closed circle in the basal plane diagram requires a fractional translation by an amount $c/2$ along the z axis, i.e., by $\mathbf{t}_3/2$, in the three dimensional structure. $\mathbf{t}_1$, $\mathbf{t}_2$, and $\mathbf{t}_3$ (not shown) denote basic vectors in the Bravais lattice. a and c (not shown) are the usual hexagonal parameters. The projection of the Brillouin zone on the k_xk_y plane in reciprocal space has sides which are parallel to the sides of the larger hexagon.

II. EXTENSION OF SYMMETRY ANALYSIS (METHOD AND RESULTS)

As is well known, for space groups without fractional translations the representations of $G^{\mathbf{k}}$ can be expressed simply in terms of the representations of $g^{\mathbf{k}}$, the point group of $G^{\mathbf{k}}$. Thus

$$D[(\alpha|\mathbf{t})]=\exp(-i\mathbf{k}\cdot\mathbf{t})d(\alpha), \tag{3}$$

where $D[(\alpha|\mathbf{t})]$ is the matrix representative of $(\alpha|\mathbf{t})$ belonging to the irreducible representation, D of $G^{\mathbf{k}}$ and d is an irreducible representation of $g^{\mathbf{k}}$. For space groups having fractional translations, Herring[5] has pointed out that at zone boundaries one must generally consider the full factor group $G^{\mathbf{k}}/T^{\mathbf{k}}$. We shall demonstrate that for the special case of wurtzite it is only necessary to find representations of $g^{\mathbf{k}}$. We proceed by a method due to Koster.[19] He has shown that in the interior of the zone

$$D[(\alpha|\mathbf{a})]=\exp(-i\mathbf{k}\cdot\mathbf{a})d(\alpha), \tag{4}$$

where $\mathbf{a}=\mathbf{v}_\alpha+\mathbf{t}$. A necessary condition[23] for D, as defined in Eq. (4), to be a representation is

$$D[(\alpha\alpha'|\alpha\mathbf{a}'+\mathbf{a})]=D[(\alpha|\mathbf{a})]D[(\alpha'|\mathbf{a}')]. \tag{5}$$

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[20] Professor Dresselhaus has kindly pointed out that while he is in error in making this assumption when applying the results of his analysis to structures of the wurtzite type, the assumption is correct when applied to tellurium, which he has also considered in reference 16 (private communication).

[21] See, for example, E. Wigner, *Gruppentheorie und ihre Andwendung, auf die Quantenmechanik der Atomspektren* (Braunschweig, 1931; Edwards Brothers, Inc., Ann Arbor, 1944).

[22] S. P. Keller and G. D. Pettit, private communication (unpublished).

[23] That Eq. (5) is also a sufficient condition for D, as defined in Eq. (4) to be an irreducible representation of the group of the wave vector follows from the fact that d is irreducible by hypothesis. Therefore, the only matrix which commutes with d and, hence, with D is a constant times the unit matrix.

TABLE I. Summary of symmetry analysis. At each point of symmetry in the zone[a] the point group, $g^{\mathbf{k}}$ associated with the factor group, $G^{\mathbf{k}}/T^{\mathbf{k}}$ is given. The characters, χ_d may be found in Koster's article.[b] The representations in most of Koster's tables are not labeled. We define the representations, d_i to be numbered consecutively. In the exceptional cases (Table V and Table LVII) where his representations are labeled, but do not appear in sequence, we follow his notation. Classes labeled σ_v in Koster's tables contain reflections which, according to the definitions in Sec. I of the present report, are associated with nonzero fractional translations. The coordinates x, y, z are defined with respect to the wurtzite lattice in Fig. 1 of the present work, if one assumes a right-handed triad.

Symmetry points in zone[a]	Point group $g^{\mathbf{k}}$	Character table reference[b] (without spin)	Representations, d contained	Character table reference[b] (with spin)	Representations, d contained	Representations occurring together due to time reversal	Representations to which r belongs	Representation(s) like $D^{1/2}$
Γ, Δ, A	C_{6v}	Table XXIV	d_1-d_6	Table LXIII	d_7-d_9	A_1 and A_3 A_2 and A_4 A_5 and A_6 A_7 and A_8 A_9 (double)	d_1, z d_5, x, y	d_7
K, P, H	C_{3v}	Table XVIII	d_1-d_3	Table LVII	d_4-d_6	H_1 and H_2 H_4 and H_5	d_1, z d_3, x, y	d_6
M, U, L	C_{2v}	Table V	d_1-d_4	Table XLV	d_5	L_1 and L_4 L_2 and L_3 L_5 (double)	d_1, z d_3, $x-\sqrt{3}y$ d_4, $\sqrt{3}x+y$	d_5
Σ, R	C_s	Table III	d_1, d_2	Table XLII	d_3, d_4	R_1 (double) R_2 (double) R_3 (double) R_4 (double)	d_1, z, $\sqrt{3}x+y$ d_2, $x-\sqrt{3}y$	d_3+d_4
T, S	C_s	Table III	d_1, d_2	Table XLII	d_3, d_4	S_1 and S_2 S_3 and S_4	d_1, z, x d_2, y	d_3+d_4
T', S'	C_s	Table III	d_1, d_2	Table XLII	d_3, d_4	S_1' and S_2' S_3' and S_4'	d_1, z, $x-\sqrt{3}y$ d_2, $\sqrt{3}x+y$	d_3+d_4

[a] See Fig. 17, reference 19.
[b] Reference 19.

At the zone boundaries one usually finds

$$D[(\alpha\alpha'|\alpha\mathbf{a}'+\mathbf{a})]$$
$$=\exp(-i\mathbf{K}\cdot\mathbf{v}_{\alpha'})D[(\alpha|\mathbf{a})]D[(\alpha'|\mathbf{a}')], \tag{6}$$

where $\mathbf{K}$ is a principal vector in the reciprocal lattice which satisfies the condition

$$\alpha^{-1}\mathbf{k}=\mathbf{k}+\mathbf{K}. \tag{7}$$

Examination of the operators, α in Eq. (1) shows that for arbitrary $\mathbf{k}$, the vector $\mathbf{K}$ defined in Eq. (7) has no component in the z direction. Thus, for our choice of coordinates $\mathbf{K}\cdot\mathbf{v}_{\alpha'}$ vanishes and Eqs. (4) and (5) hold at the zone boundaries as well as in the interior. Since the translational part of an operator has no effect on the spin, it is clear that a similar proof holds for the double group. Thus, we need find only the characters of the representations of the point groups $g^{\mathbf{k}}$. From Eq. (4) it follows that the characters χ_D and χ_d are related by the expression

$$\chi(D,[(\alpha|\mathbf{a})])=\exp(-i\mathbf{k}\cdot\mathbf{a})\chi(d,\alpha). \tag{8}$$

As the character tables for the point groups are well known, it is not necessary to reproduce them here. A summary of the results of the analysis is contained in Table I. Although Table I is self contained, a few additional comments might be made.

1. Since we have not included the character tables of the point groups, a standard reference is necessary for notational purposes. We have selected the review article by Koster.[19]

2. With the single exception that p_z transforms according to the identity representation, the character table at $\mathbf{k}=0$ is identical with Table I in reference 16.

3. When the Wigner-Herring test[6,7] implies extra degeneracies due to time-reversal symmetry, it may happen that energy bands belonging to two representations, D and $\bar{D}$, stick together at certain points or along certain lines in the zone. Moreover, as was noted by Elliott,[9] $\bar{D}$ is not in general simply the complex conjugate of D. In Table I we have listed the representations d and $\bar{d}$ which coalesce. $\bar{d}$ is defined by the relation

$$\bar{D}[(\alpha|\mathbf{a})]=\exp(-i\mathbf{k}\cdot\mathbf{a})\bar{d}(\alpha). \tag{9}$$

The associated representations D and $\bar{D}$ may be found via Eq. (8) and the following expression which results from Eq. (9):

$$\chi(\bar{D},[(\alpha|\mathbf{a})])=\exp(-i\mathbf{k}\cdot\mathbf{a})\chi(\bar{d},\alpha). \tag{10}$$

For D and $\bar{D}$ to occur together it is necessary that $-\mathbf{k}$ be in the star[4] of $\mathbf{k}$. Since wurtzite is polar this can happen only at the top surface of the zone[24] where $-\mathbf{k}$ can be equivalent to $\mathbf{k}$ and in the plane $k_z=0$. In the plane $k_z=0$, there is no extra degeneracy. In the interior and on the sides of the zone, the Kramers degeneracy implies $E(-\mathbf{k})=E(\mathbf{k})$ but does not cause two bands to stick together at a given value of $\mathbf{k}$.

4. From the information in Table I and reference 19

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[24] A figure showing the zone shape as well as the points of symmetry may be found in references 5, 9, or 19.

one can readily determine[25] whether or not $\text{grad}_{\mathbf{k}}E(\mathbf{k})$ vanishes at various points in the zone as a result of the spatial symmetry. As is well known, when a finite slope is indicated, one must investigate further to see whether the slope must vanish as a consequence of the time-reversal symmetry. We shall resolve this question in detail only at the origin of the zone, i.e., at the point Γ. Examination of Table I and the relevant tables referred to therein indicates a finite slope in the k_z direction for bands associated with all representations and in the k_xk_y plane for the extra representations, Γ_7 and Γ_8 of the double group. Actually, the slope vanishes in the k_z direction for all representations. This is seen readily from the fact that a finite slope would imply a discontinuity in slope at the origin in the curve depicting $E(\mathbf{k})$ for values of $\mathbf{k}$ lying along the k_z axis, since $E(-k_z)=E(k_z)$ and since the degeneracy is not lifted as one proceeds away from the origin in the k_z direction. By constructing explicit functions which transform according to Γ_7 and Γ_8, it was found that the slope also vanishes for $\mathbf{k}$ in the k_xk_y plane, to first order in the spin-orbit interaction, if the $\mathbf{r}$-dependence of the spinor components is characterized by transformation properties associated with the two-dimensional representations, Γ_5, Γ_6 of the point group without spin. That is, $\Gamma_7(\Gamma_5)$ and $\Gamma_8(\Gamma_6)$ are associated with bands having zero slope at the origin. Bands associated with $\Gamma_7(\Gamma_1)$, $\Gamma_7(\Gamma_2)$, $\Gamma_8(\Gamma_3)$, and $\Gamma_8(\Gamma_4)$ have finite slopes. For these cases it was found that the energy, to first order in $\mathbf{k}$, is proportional to $k \sin\theta$ in spherical coordinates. Finite slopes can occur when spin-orbit coupling is taken into account as the appropriate perturbation for this case is not simply $\mathbf{k}\cdot\mathbf{p}$, but includes an additional term[25] proportional to $\mathbf{k}\cdot(\boldsymbol{\sigma}\times\nabla V)$.

5. Since the representations are, at most, two-dimensional for the wurtzite structure, compatibility relations of the type first considered by Bouckaert, Smoluchowski, and Wigner[4] can be obtained at once by inspection of the character tables; hence, they are omitted.

III. OPTICAL SELECTION RULE

A derivation of the selection rule stated in Sec. I is outlined. Following Dresselhaus,[16] the wave function associated with a wave vector, $\mathbf{k}$, which is in the neighborhood of the origin of the zone, is expressed in terms of the eigensolutions at $\mathbf{k}=0$ via the $\mathbf{k}\cdot\mathbf{p}$ perturbation. Consider an optical transition from band i to band f. The band extrema are assumed to lie at $k=0$. At the origin, the wave functions ψ_i^0 and ψ_f^0 associated with these bands are assumed to belong to representations Γ_i and Γ_f, respectively. In the neighborhood of the origin $\psi_i^{\mathbf{k}}$ and $\psi_f^{\mathbf{k}}$, the periodic parts of the wave functions, will be predominantly of the type Γ_i and Γ_f but will contain admixtures of other states. Which states are admixed to various orders in the perturbation parameter, k can be ascertained by standard group theoretical methods. $\psi_i^{\mathbf{k}}$ and $\psi_f^{\mathbf{k}}$ are treated as zeroth order solutions in a second perturbation calculation where the electromagnetic interaction, proportional to $\boldsymbol{\varepsilon}\cdot\mathbf{p}$, is the perturbing term in the Hamiltonian. For each choice of Γ_i and Γ_f, except $\Gamma_i=\Gamma_f$, it was found that if the lowest order matrix element $(\psi_i^{\mathbf{k}}|\boldsymbol{\varepsilon}\cdot\mathbf{p}|\psi_f^{\mathbf{k}})$ is of order k^n for light polarized perpendicular to the c axis, the lowest order matrix element for light polarized along the c axis is of order k^{n+1}. The result was obtained only to first order in the spin-orbit coupling.

We have shown in Sec. II that nonzero slopes in $E(\mathbf{k})$ can occur at $\mathbf{k}=0$ for bands associated with certain representations as a result of the spin-orbit coupling. When this happens, a band extremum which occurs at $\mathbf{k}=0$ in the absence of the coupling will be displaced away from the origin in its presence, giving rise to several extrema clustered about the origin. We have assumed that when finite slopes can occur at $\mathbf{k}=0$ they are quite small, that is, for reasonable curvatures, that the extrema will lie sufficiently close to the origin for an expansion of the wave functions in terms of the solutions at $\mathbf{k}=0$ to be useful. Under this assumption, the analysis outlined in the previous paragraph is applicable, even though the band extrema do not lie precisely at the origin. For InSb Dresselhaus[11] has estimated that the linear term in $E(\mathbf{k})$ at $\mathbf{k}=0$ is sufficiently small that when extrapolated to the zone boundary it results in an energy displacement of only about 0.02 ev. If the slopes in CdS and ZnS are of the same order of magnitude as in InSb, his estimate appears consonant with our assumption.

For any given material it may happen that one or more of the band extrema lie quite distant from the origin of the zone, even though the linear term in $E(\mathbf{k})$ vanishes at $\mathbf{k}=0$, as in Ge and Si where indirect transitions are important. In their theory of indirect transitions, Bardeen, Blatt, and Hall[26,27] have considered two contributing processes: (a) a process in which an electron is first excited from the region of maximum energy in the valence band (near $\mathbf{k}=0$) to an intermediate state in the conduction band (also near $\mathbf{k}=0$) and then is scattered by a phonon into a region of minimum energy in the conduction band (away from $\mathbf{k}=0$), (b) a process in which an electron is first excited from the valence band (away from $\mathbf{k}=0$) to a region of minimum energy in the conduction band (also away from $\mathbf{k}=0$) such that $\mathbf{k}$ is conserved and then the resulting hole is scattered into the region of maximum energy in the valence band (near $\mathbf{k}=0$). In applying their results to solids having the wurtzite structure, we assume that the valence band maximum lies at $\mathbf{k}=0$ as in Ge and Si. Under this assumption, we expect the selection rule to apply only if the (b)

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[25] See, for example, reference 11.

[26] Bardeen, Blatt, and Hall, *Proceedings of the Photoconductivity Conference, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 146.

[27] Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954).

process contributes negligibly to the absorption in comparison with the (a) process. Hence, we are unable to draw rigid conclusions regarding the applicability of the rule to indirect transitions without a detailed knowledge of the band structure of a specific solid.

Recently Balkanski and Waldron[28] have studied the CdS and ZnS systems experimentally. Their absorption curves for CdS are in agreement with the selection rule in the fundamental region. The absorption for long wavelengths, which is dependent upon impurity content, exhibits a violation of the rule. As the authors have noted, one cannot expect band-to-band selection rules to apply at these wavelengths. For this reason, since their data for ZnS do not extend into the fundamental region, their results, which happen to agree with the rule, cannot be interpreted within the framework of the present analysis without additional assumptions. As mentioned earlier, the rule is verified for ZnS by the work of Piper *et al.*[14] and Keller and Pettit[22] whose measurements extend well into the region of fundamental absorption.

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Temperature Dependence of the Electrical Properties of Bismuth-Antimony Alloys*†

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The electrical resistivity ρ and Hall effect R of zone-levelled single crystals of Bi-Sb alloys have been measured in the temperature range from 4.2°K to 300°K. $\mathrm{Log}(\rho/\rho_{300})$ *vs* $1/T$ curves suggest thermal activation of carriers in the concentration range from 5% to 40% Sb in the temperature range from 25°K to 100°K; approximate activation energies have been inferred from their slopes. The activation energy appears to have a maximum at a concentration near 12%. Some anomalies have been observed in the behavior of ρ and R on both sides of this concentration at low temperatures. Lattice parameters for these alloys have also been measured for the entire range of solid solubility. Both a maximum and minimum in the c-axis lattice parameter *vs* concentration occur near the concentration at which anomalies appear in transport properties. These phenomena are discussed in terms of a simple band model proposed by Blount and Cohen.

I. INTRODUCTION

RHOMBOHEDRAL bismuth is a semimetal with a carrier concentration of about $10^{18}/\mathrm{cm}^{-3}$. Some information concerning the band structure has been obtained from measurements of de Haas-van Alphen effect,[1] cyclotron resonance,[2] galvanomagnetic[3] effects, and elastoresistance.[4] These effects have been interpreted in terms of the conduction band overlapping upon the valence band by 0.0184 ev. This overlap gives rise to the small number of electrons in the conduction and an equal number of holes in the valence band. The experimental results are all consistent with a Fermi surface composed of a set of 3 ellipsoids for electrons and an ellipsoid of revolution around the trigonal axis for holes. The three ellipsoids can be transformed into one another by 120° rotations around the trigonal axis. Combining the de Haas-van Alphen effect data with their specific heat data at low temperatures, Kalinkina and Strekov[5] have determined the mean effective mass of holes to be $m_h^* \cong 2.5m_0$ which is very large compared to that of electrons $m_e^* \cong 0.05m_0$ given by Shoenberg.[1]

Further information about the band structure in bismuth can be obtained from the electrical and magnetic properties of its alloys. It was realized by Jones[6] that alloying bismuth with small amounts of elements with different valence might permit the study of either an electron band or a hole band separately. Thompson[7] has indeed carried out above 15°K extensive measurements of the electrical properties of bismuth alloys containing Pb, Sn, Se, Te, as well as less extensive studies of other alloys. The group IV elements Pb and Sn act as acceptors much as do group III elements in the silicon-germanium type of semiconductor. Similarly,

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