Band Structure of Solid Argon*

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The orthogonalized plane wave method, in a perturbation approximation recently introduced by Bassani and Celli, is used to compute the lowest lying conduction states in (fcc) solid argon at the symmetry points Γ, X, L, and K. The $3s$ and $3p$ valence bands are treated by tight-binding theory. The potential used in the computation consists of a sum of effective atomic potentials in which a free-electron-like expression is used for the exchange contribution. The lowest conduction state appears to be s-like (Γ_1), lying 12.4 ev above the highest valence state (Γ_{15}). The results of the computation are compared with present theoretical and experimental knowledge of the electronic structure of the solid rare gases.

I. INTRODUCTION

THE thermal and mechanical properties of the solid rare gases have been studied for many years, but only recently has experimental investigation of their optical properties been undertaken.[1] These crystals are expected to be excellent insulators and are transparent to visible and near-uv light. We feel that an investigation of their band structure along the lines of the elementary one-electron approximation is of interest because no comparable study has been made, and because such a calculation might give some indication of the conduction band structure of more complicated solids such as ionic crystals, which also consist of closed-shell atoms. A calculation of the $3p$ valence band of NaCl has been made by Casella,[2] using a model of an argon sublattice. More recently one of us[3] has computed the exciton band structure of solid argon, using the Frenkel model.

In the present paper we make an attempt to calculate the electronic band structure of solid argon in the one-electron approximation. We find it necessary to use different methods for valence and conduction states. For the former we use the tight-binding approximation; the procedure and calculations are described in Sec. II. For the conduction band we use the second-order perturbation approximation developed in a series of papers by Bassani and Celli.[4,5] This is related to but simpler than the conventional orthogonalized plane wave (OPW) method and usually gives equivalent results. The conduction-band calculation is described in Sec. III. Section IV contains a brief discussion of the results as they relate to the optical properties of solid argon.

II. VALENCE BANDS

The total one-electron Hamiltonian used in all parts of this calculation was taken to be

$$H = p^2/2m + \sum_\nu V_a(\mathbf{r} - \mathbf{R}_\nu), \qquad (1)$$

in which $V_a(\mathbf{r} - \mathbf{R}_\nu)$ is an effective potential due to a single argon atom located at the lattice point $\mathbf{R}_\nu$, and the sum runs over all lattice points. V_a consists of a Coulomb part derived from the Hartree-Fock atomic charge density[6] and an average exchange potential[7] first computed for argon by Casella.[2] Our valence-band calculation is in fact quite similar to Casella's treatment of a fictitious argon crystal in connection with the valence bands of NaCl; nearest-neighbor tight-binding theory was used in treating the $3s$ and $3p$ bands, but all bands lying below $3s$ were considered flat. (In Sec. III we shall refer to the former as the "valence" states and to the latter as "core" states.)

It is convenient to work with explicitly normalized valence band functions, e.g.,

$$\psi_{3s}(\mathbf{k}) = [NO_{3s}(\mathbf{k})]^{-\frac{1}{2}} \sum_\nu \exp(i\mathbf{k}\cdot\mathbf{R}_\nu) u_{3s}(\mathbf{r} - \mathbf{R}_\nu), \quad (2)$$

where N is the number of cells in the crystal, $u_{3s}(\mathbf{r} - \mathbf{R}_\nu)$ is the atomic Hartree-Fock $3s$ function centered at the lattice point ν, and

$$O_{3s}(\mathbf{k}) = \sum_\nu \exp(i\mathbf{k}\cdot\mathbf{R}_\nu)(u_{3s}(\mathbf{r}), u_{3s}(\mathbf{r} - \mathbf{R}_\nu)). \quad (3)$$

Similarly, for the p bands, we use normalized symmetry-adapted linear combinations

$$\psi_{3p}{}^\alpha = [NO_{3p}{}^\alpha(\mathbf{k})]^{-\frac{1}{2}} \sum_m c_m{}^\alpha(\mathbf{k})$$
$$\times \sum_\nu \exp(i\mathbf{k}\cdot\mathbf{R}_\nu) u_{3pm}(\mathbf{r} - \mathbf{R}_\nu) \quad (4)$$

in which the u_{3pm} are the atomic p functions, $O_{3p}{}^\alpha(\mathbf{k})$ is

[1] O. Schnepp and K. Dressler, J. Chem. Phys. 33, 49 (1960); G. O. Jones and B. L. Smith, Phil. Mag. 5, 355 (1960).

[2] R. C. Casella, Phys. Rev. 104, 1260 (1956).

[3] R. S. Knox, J. Phys. Chem. Solids 9, 265 (1959).

[4] F. Bassani and V. Celli, Nuovo cimento 11, 805 (1959); Studia Ghisleriana 2, 157 (1959).

[5] F. Bassani and V. Celli, J. Phys. Chem. Solids (to be published).

[6] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A166, 450 (1938).

[7] J. C. Slater, Phys. Rev. 81, 385 (1951).

TABLE I. Two-center integrals evaluated at a nearest-neighbor separation of $R=2^{-\frac{1}{2}}a=7.10a_0$. Here u_{nlm} is a Hartree-Fock atomic function and V_a is the effective atomic potential described in the text.

nlm	$(u_{nlm}(\mathbf{r}), u_{nlm}(\mathbf{r}-\mathbf{R}))$	$(u_{nlm}(\mathbf{r}), V_a(\mathbf{r})u_{nlm}(\mathbf{r}-\mathbf{R}))$	$(u_{nlm}(\mathbf{r}), V_a(\mathbf{r}-\mathbf{R})u_{nlm}(\mathbf{r}))$
$3s\sigma$	$+0.00229$	-0.00140 ry	-0.0276 ry
$3p\sigma$	-0.0269	$+0.01554$	-0.0364
$3p\pi$	$+0.00438$	-0.00202	-0.0252
$4s\sigma$	$+0.55$	$\cdots$	$\cdots$

again a normalization factor, and the coefficients $c_m^\alpha(k)$ transform the unsymmetrized Bloch functions into basis functions of the irreducible representation α of the small group of $\mathbf{k}$.

We have evaluated matrix elements of H between all pairs of states of the form (2) and (4), neglecting three-center terms and two-center terms involving other than nearest neighbors. Also evaluated were the overlap terms $(\psi_{3s}{}^\alpha, \psi_{3p}{}^\alpha)$, which are of great importance in connection with mixing of the $3s$ and $3p$ bands. Lattice sums necessary for these calculations have been published by Slater and Koster[8]; numerical values of the two-center integrals used are shown in Table I. A lattice constant (cube edge) of $a=10.05a_0=5.33$ A, corresponding to a density at 20°K of 1.764 g cm^{-3} as measured by Dobbs et al.,[9] was used. The small overlap between wave functions on second-nearest neighbors justifies our nearest-neighbor approximation. For example, the $3p\sigma$-$3p\sigma$ overlap at $R=a$ is -0.0021,[3] compared with the nearest-neighbor value -0.0269.

The results of the valence-band calculation are listed in Table II and sketched in Fig. 1. As expected, the computed $3p$ bands closely resemble Casella's bands[2]; however, they are slightly narrower in spite of the slightly smaller lattice constant of solid argon compared with that of NaCl, because we have included overlap in our calculation. As pointed out below, mixing between the $3s$ and $3p$ bands was found to have a negligible effect on their energies. Hartree-Fock eigenvalues[6] have been used in positioning the $3s$ and $3p$ valence bands in Table II and Fig. 1, and in locating the core bands in the OPW formalism (Sec. III). We have thus assumed that the Hartree-Fock functions are good eigenfunctions of our effective atomic Hamiltonian, with the Hartree-Fock eigenvalues. Although this is certainly not the case with our choice of effective exchange potential,[10] we feel confident that the error thus introduced will be small. This is justified by the following considerations. We have verified that coupling between the $3s$ and $3p$ bands is negligible along all lines of high symmetry and at the point K, where the possibility of mixing between the two K_1 levels exists. Let us however compute the matrix element responsible for the mixing at the point K in two ways using the Hermitian property of H and using the assumption mentioned above, i.e., that the Hartree-Fock functions are eigenfunctions of $p^2/2m+V_a$. We obtain

$$(\psi_{3p}(K_1), H\psi_{3s}(K_1)) = A\epsilon_{3s}+B$$
$$= A\epsilon_{3p}+C, \qquad (5)$$

where A, B, and C are various linear combinations of overlap and other two-center integrals involving the effective potential, a $3s$ function at one center, and a $3p\sigma$ function on the other. The two forms have computed values $-0.0207i$ and $-0.0203i$, respectively; we take this close agreement as an indication that the potential seems fairly accurate for computing two-center integrals in the valence-band structure calculations.

The spin-orbit term of the Hamiltonian has been ignored, as in earlier calculations of chloride valence bands. The most noticeable effect of the spin-orbit interaction will be a splitting of the $3p$ valence band at Γ into two bands (Γ_6 and Γ_8), separated by about 0.1 ev. The limited objectives of the present work do not warrant a specific calculation of this effect.

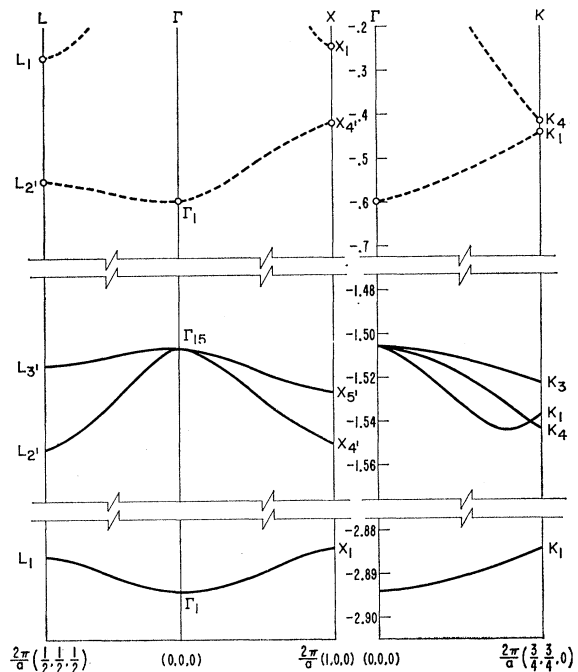At an early stage of this work an attempt was made

FIG. 1. Band structure of solid argon. Energy is in rydbergs, measured relative to the energy of an electron at rest at infinity. Note changes of scale between bands.

[8] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
[9] E. R. Dobbs, B. F. Figgins, G. O. Jones, D. C. Peircey, and D. P. Riley, Nature 178, 483 (1956).
[10] See, e.g., D. R. Hartree, Phys. Rev. 109, 840 (1958).

TABLE II. Computed energies (in rydbergs) at the symmetry points Γ, X, L, and K in the reciprocal lattice of fcc argon (cube edge $=10.05a_0$). Eigenvalues for the $1s$, $2s$, and $2p$ core states are -237.2, -24.65, and -19.15 ry, respectively. Also included are the normalization coefficients $O_{nl}(\mathbf{k})$ for valence-band Bloch states. Notation for the symmetry types is that of Bouckaert, Smoluchowski, and Wigner.[a]

Band	Γ_1	$\Gamma_{2'}$	Γ_{15}	$\Gamma_{25'}$	X_1	$X_{4'}$	$X_{5'}$	K_1	K_3	K_4	L_1	$L_{2'}$	$L_{3'}$
$3s$	-2.894	$\cdots$	$\cdots$	$\cdots$	-2.884	$\cdots$	$\cdots$	-2.884	$\cdots$	$\cdots$	-2.886	$\cdots$	$\cdots$
$3p$	$\cdots$	$\cdots$	-1.506	$\cdots$	$\cdots$	-1.550	-1.526	-1.536	-1.522	-1.544	$\cdots$	-1.552	-1.514
Cond.	-0.597	$+0.152$	$+0.414$	-0.031	-0.243	-0.422	$\cdots$	-0.439	$\cdots$	-0.415	$\cdots$	-0.268	-0.553
O_{3s}	1.027	$\cdots$	$\cdots$	$\cdots$	0.991	$\cdots$	$\cdots$	0.992	$\cdots$	$\cdots$	1.000	$\cdots$	$\cdots$
O_{3p}	$\cdots$	$\cdots$	0.927	$\cdots$	$\cdots$	1.108	0.983	1.028	0.966	1.073	$\cdots$	1.125	0.937

[a] L. P. Bouckaert, R. Smoluchowski, and E. P. Wigner, Phys. Rev. **50**, 58 (1936).

to compute the obviously tightly bound $3s$ and $3p$ valence bands using the OPW formalism of Sec. III. This attempt failed, predicting metallic argon at the normal lattice spacing.

III. THE CONDUCTION BAND

The energy levels of the conduction band cannot be calculated in the tight-binding approximation, because the argon $4s$ atomic function is greatly extended in space relative to the valence wave functions[11] and the overlap of these functions centered on different atoms is very large (0.55 for nearest neighbors!). This is not surprising, since from the high ionization potential of atomic argon (15.8 ev) we expect a rather large energy gap for solid argon and consequently a nearly-free-electron wave function for the conduction band.

To calculate the energy levels of the conduction band we expand the wave function in crystal symmetry combinations of plane waves (CSCPW) belonging to a given row of a given irreducible representation of the small group of $\mathbf{k}$, with the additional requirement that the final wave function be orthogonal to the states of lower energy. The Schrödinger equation is then solved for the energy by second-order perturbation theory[5] rather than by the variational theorem as in the complete orthogonalized plane wave (OPW) method.[12]

As discussed in reference 5, the unperturbed states are the solutions of the "empty lattice" problem. The corresponding eigenfunctions are CSCPW's denoted by $S_p{}^\alpha$, as described in the Appendix, and the corresponding eigenvalues are taken to be

$$|\mathbf{k} + \mathbf{h}_i|^2 + V(0), \qquad (6)$$

where $V(0)$ is the space average of the crystal potential and $\mathbf{h}_i$ is any reciprocal lattice vector of the set from which $S_p{}^\alpha$ is constructed. An effective perturbation potential R can be written as an operator on any set of plane waves and in our case it also includes terms due to orthogonalization to the valence as well as to core states. We have

$$RS_p{}^\alpha \equiv [V_c - V(0)]S_i{}^\alpha + \sum_c (E^\alpha - E_c)(\psi_c{}^\alpha, S_p{}^\alpha)\psi_c + \sum_v (E^\alpha - E_v)(\psi_v{}^\alpha, S_p{}^\alpha)\psi_v, \qquad (7)$$

where V_c is the total crystal potential [cf. Eq. (1)]

$$V_c = \sum_\nu V_a(\mathbf{r} - \mathbf{R}_\nu), \qquad (8)$$

$\psi_c{}^\alpha$ and $\psi_v{}^\alpha$ are eigenfunctions of the core and valence states, respectively, with eigenvalues E_c and E_v, the first summation extends over the core states and the second over the valence states, and E^α is the desired eigenvalue.

Matrix elements $(S_q{}^\alpha, RS_p{}^\alpha)$ are used in the perturbation approach; they are evaluated to first order by letting $E^\alpha = E_0{}^\alpha$, where $E_0{}^\alpha$ is the unperturbed eigenvalue (6), and to second order by letting $E^\alpha = E_0{}^\alpha + E_1{}^\alpha$, where $E_1{}^\alpha$ is the first-order correction to the energy. A formula is given in the Appendix to express $(S_q{}^\alpha, \psi_v{}^\alpha) \times (\psi_v{}^\alpha, S_p{}^\alpha)$ in terms of the standard[12] orthogonality coefficients $A_{nl}(|\mathbf{k} + \mathbf{h}_i|)$.

The calculation has been done at the points Γ, X, L, and K of the reduced zone. The CSCPW's for the fcc lattice have been obtained, in the way described by Herman[13]; typical such combinations of plane waves have been given by Casella.[14] We use only those sets of unperturbed states having energies up through $11(2\pi/a)^2 + V(0)$ and then obtain, to second order of perturbation theory, explicit expressions for the energies. For example, the energy of the lowest conduction state so computed is

$$E(\Gamma_1) = V(0) + \{\sum_n [V(0) - E_{ns}]O_{ns}^{-1}|A_{ns}(0)|^2\}\{1 + \sum_n O_{ns}^{-1}|A_{ns}(0)|^2\}$$
$$- 8|V(3) + \sum_n [V(0) - E_{ns}]O_{ns}^{-1}A_{ns}(0)A_{ns}(3)|^2/3(2\pi/a)^2$$
$$- 6|V(4) + \sum_n [V(0) - E_{ns}]O_{ns}^{-1}A_{ns}(0)A_{ns}(4)|^2/4(2\pi/a)^2$$
$$- 12|V(8) + \sum_n [V(0) - E_{ns}]O_{ns}^{-1}A_{ns}(0)A_{ns}(8)|^2/8(2\pi/a)^2$$
$$- 24|V(11) + \sum_n [V(0) - E_{ns}]O_{ns}^{-1}A_{ns}(0)A_{ns}(11)|^2/11(2\pi/a)^2. \qquad (9)$$

[11] R. S. Knox, Phys. Rev. **110**, 375 (1958).
[12] C. Herring, Phys. Rev. **57**, 1169 (1940); T. O. Woodruff in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 367.
[13] F. Herman, Phys. Rev. **93**, 1214 (1954).
[14] R. C. Casella, Phys. Rev. **109**, 54 (1958).

TABLE III. Fourier coefficients of the crystal potential in rydbergs. $V(p)$ is defined in connection with Eq. (10) of the text.

p	0	3	4	8	11	12	16	19	20
$V(p)$	-1.578	-0.432	-0.366	-0.242	-0.200	-0.189	-0.158	-0.141	-0.136

TABLE IV. Selected values of orthogonality coefficients. $A_{nl}(p)$ stands for $A_{nl}(|\mathbf{k}+\mathbf{h}_i|)$ in the case $|\mathbf{k}+\mathbf{h}_i|^2 = p(2\pi/a)^2$.

p	0	3	4	8	11
$A_{1s}(p)$	0.01252	0.01242	0.01238	0.01225	0.01215
$A_{2s}(p)$	-0.09847	-0.08878	-0.08582	-0.07516	-0.06825
$-iA_{2p}(p)$	0	0.03636	0.04059	0.05041	0.05390
$A_{3s}(p)$	0.6026	0.2072	0.1497	0.0373	0.0054
$-iA_{3p}(p)$	0	-0.3867	-0.3245	-0.1680	-0.1078

The summations extend over all core and valence states of symmetry Γ_1 (s-like). For convenience we have used the abbreviation $V(p)$ to stand for the Fourier coefficient

$$V(\mathbf{h}) = \Omega^{-1} \int V_a(\mathbf{r}) e^{-i\mathbf{h}\cdot\mathbf{r}} d\mathbf{r} \qquad (10)$$

in the case $\mathbf{h}^2 = p(2\pi/a)^2$. In Eq. (10), Ω is the volume of the unit cell and the integral extends over the whole crystal. A similar abbreviation is used in $A_{nl}(p)$.

The Fourier coefficients $V(p)$ were evaluated from the analytic approximation to $V_a(\mathbf{r})$ given by Casella and are listed in Table III. The orthogonality coefficients were obtained by numerical integration directly from the atomic functions,[6] and are listed in Table IV. They have been calculated at other points but these results are not tabulated because for all practical purposes they can be reproduced from Table IV by interpolation and extrapolation. The energies of the core states are taken as the Hartree-Fock eigenvalues but the energies of the valence states and their normalization constants are taken from the valence-band calculation of Sec. II and can be found in Table II. It is understood that $O_{1s} = O_{2s} = O_{2p} = 1$.

The results for the lowest conduction band levels are included in Table II and Fig. 1. The minimum of the conduction band appears to be at the center of the reduced zone and corresponds to a totally symmetric state Γ_1. At the points X and L, however, the p-like states $L_{2'}$ and $X_{4'}$ are lower than the s-like states X_1 and L_1. The forbidden energy gap for solid argon is smallest at the point Γ and is about 12.4 ev. The "electron affinity," or depth of the conduction band minimum below the vacuum, is about 6.6 ev.

It is very difficult to estimate the accuracy of our results because of the approximations involved in the perturbation procedure and because of the approximate nature of the potential chosen. In the perturbation calculation the second-order terms arising from the matrix elements $(S_q{}^\alpha, RS_p{}^\alpha)$ with $q \neq p$ are very small compared with the energy denominators and this points to good convergence. The reason lies in a cancellation between the Fourier coefficients of the potential and the

terms which arise from orthogonalization to the inner states, as recently pointed out by various authors.[4,13,15] This is particularly true in the case of the lowest conduction state Γ_1, but for higher states the cancellation becomes much less effective. A greater source of error lies in the choice of the potential which is only approximately consistent with wave functions and eigenvalues of atomic argon, as discussed in Sec. II. However, we are dealing with a closed-shell atom and expect the approximation to exchange to be much better than in the case of metals and semiconductors, where it was previously used.[16] The value of $V(0)$ obtained by direct integration of the potential appears to be reasonable and not too large by a factor of about 3 as it has been found to be for open-shell atoms (see Woodruff, reference 12). A better approximation to the potential may decrease the value of $V(0)$ by as much as 20% and produce an increase in the energy gap of the order of 2 ev, but we do not expect it to change the details of the band structure.

IV. DISCUSSION

Very little experimental information on the optical properties of solid argon is available. The work of Schnepp and Dressler[1] supplies some clue as to what one can expect, however. They find no optical absorption in argon whatsoever up through photon energies of 10 ev, but in two other rare gas films (Kr,Xe) strong absorption bands are observed at wavelengths corresponding very nearly to the energies of the first excited states of atomic Kr and Xe. It is probable that these bands can be attributed to exciton absorption and that a similar phenomenon will be observed in solid argon, i.e., exciton absorption will occur somewhere in the vicinity of 11.5 to 12.0 ev. Clearly, experiments are necessary to confirm this extrapolation which is not inconsistent with our band gap of 12.4 ev. Traditionally

[15] E. Antončik, Czech. J. Phys. 4, 439 (1954); J. C. Phillips and L. Kleinmann, Phys. Rev. 116, 287 (1959); M. H. Cohen and V. Heine, ibid. 122, 1821 (1961).

[16] See J. Callaway, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, especially pp. 107–108.

the rare-gas solids have been regarded as "tightly bound" crystals, even in discussions of exciton states. However, it is not yet known decisively whether tight- or weak-binding exciton theory is appropriate.[17]

At higher photon energies strongly allowed band-to-band transitions can take place, giving rise to an absorption edge and accompanying photoconductivity. It is of course easy to suggest many standard experiments to verify the argon band structure but it will be hard to convince experimentalists of the ease of performing them at the wavelengths involved (~ 1000 A).

We feel that calculations of effective masses directly from the band structure would be unreliable at the present stage since they are too sensitive to the details of the E versus k curves near the extrema. However, one may roughly guess from the widths of the bands in the (100) direction that the $3p$ valence-band effective masses are 1.8 and 4 electron masses. In the conduction band, the (100) effective mass, as estimated using a nearly-free electron approximation, is roughly 1.0 to 1.5 electron masses.

Besides the specific predictions of the energy gap and band structure of argon, our results indicate that a similar attempt might be made with some chance of success in ionic crystals, and we are now planning work along these lines. Our experience with argon suggests that the lowest conduction state as computed by the OPW method will also be the s-like state Γ. This would be in agreement with the only available calculations on ionic crystal conduction bands, both done by the cellular method (LiF [18] and NaCl [19]). We are aware that the polaron effect will be important in ionic crystals, but feel that an attack on the "bare" particle states is essential in view of the general lack of knowledge in this area.

Note added in proof. Subsequent to preparing this manuscript, the authors located two more calculations pertaining to conduction bands in ionic crystals. Kawamura[20] computed the eigenvalue and deformation potential at Γ in KCl by the cellular method and Tolpygo and Tomasevich[21] treated the lowest conduction band in NaCl by the tight binding method. Because of difficulties generated by large overlapping of wave functions in each of these calculations, we still suspect that an OPW calculation will be of considerable interest.

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APPENDIX

Let a crystal symmetry combination of plane waves be

$$S_p{}^\alpha = (N\Omega)^{-\frac{1}{2}} \sum_j a_{pj}{}^\alpha \exp[i(\mathbf{k}+\mathbf{h}_j)\cdot\mathbf{r}]. \quad (A1)$$

The index α refers to a given column of a given irreducible representation of the small group of $\mathbf{k}$ and the coefficients $a_{pj}{}^\alpha$ are determined by group theory with the condition $\sum_j |a_{pj}{}^\alpha|^2 = 1$. Ω is the volume of a unit cell and N is the number of unit cells; the function is, therefore, normalized over the volume of the crystal.

The wave function for a valence state is written

$$\psi_{nl}{}^\alpha(\mathbf{k},\mathbf{r}) = [NO_{nl}{}^\alpha(\mathbf{k})]^{-\frac{1}{2}}$$
$$\times \sum_m c_{lm}{}^\alpha \sum_\nu \exp(i\mathbf{k}\cdot\mathbf{R}_\nu) u_{nlm}(\mathbf{r}-\mathbf{R}_\nu). \quad (A2)$$

$O_{nl}{}^\alpha(\mathbf{k})$ is a normalization factor which is equal to 1 in the case of nonoverlapping core states. The coefficients $c_{lm}{}^\alpha$ are determined by symmetry at special $\mathbf{k}$ points or by solving a secular equation; except for the numerical factor $[O_{nl}{}^\alpha(\mathbf{k})]^{-\frac{1}{2}}$ they define a unitary transformation from the unnormalized wave functions

$$\psi_{nlm}(\mathbf{k},\mathbf{r}) = N^{-\frac{1}{2}} \sum_\nu \exp(i\mathbf{k}\cdot\mathbf{R}_\nu) u_{nlm}(\mathbf{r}-\mathbf{R}_\nu).$$

From Eqs. (A1) and (A2) we obtain

$$(\psi_{nl}{}^\alpha, S_p{}^\alpha) = [O_{nl}{}^\alpha(\mathbf{k})]^{-\frac{1}{2}} \sum_j a_j{}^\alpha \sum_m c_{lm}{}^\alpha$$
$$\times \int e^{i(\mathbf{k}+\mathbf{h}_j)\cdot\mathbf{r}} u_{nlm}(\mathbf{r})^* d\mathbf{r}. \quad (A3)$$

The integral can be evaluated in terms of orthogonality coefficients $A_{nl}(|\mathbf{k}+\mathbf{h}_j|)$ by expanding the exponential in spherical harmonics and by using the orthogonality of the associated Legendre functions; one obtains

$$(\psi_{nl}{}^\alpha, S_p{}^\alpha) = [O_{nl}{}^\alpha(\mathbf{k})]^{-\frac{1}{2}} \sum_j a_{pj}{}^\alpha [4\pi/(2l+1)]^{\frac{1}{2}}$$
$$\times \sum_m c_{lm}{}^\alpha Y_{lm}(\theta_j,\phi_j) A_{nl}(|\mathbf{k}+\mathbf{h}_j|). \quad (A4)$$

The angles ϕ_j and θ_j refer to the vector $\mathbf{k}+\mathbf{h}_j$. The expression for the orthogonality coefficients is[12]

$$A_{nl}(|\mathbf{k}+\mathbf{h}_j|)$$
$$= i^l \left[\frac{4\pi}{(2l+1)\Omega} \right]^{\frac{1}{2}} \int_0^\infty r j_l(|\mathbf{k}+\mathbf{h}_j|r) P_{nl}(r) dr. \quad (A5)$$

$P_{nl}(r)$ is the usual radial part of the atomic wave function multiplied by r. The quantities which are needed to obtain the matrix elements are

$$(S_q{}^\alpha, \psi_{nl}{}^\alpha)(\psi_{nl}{}^\alpha, S_p{}^\alpha)$$
$$= [O_{nl}{}^\alpha(\mathbf{k})]^{-1} \sum_i \sum_j a_{qi}{}^{\alpha*} a_{pj}{}^\alpha$$
$$\times A_{nl}(|\mathbf{k}+\mathbf{h}_i|)^* A_{nl}(|\mathbf{k}+\mathbf{h}_j|)$$
$$\times [4\pi/(2l+1)] \sum_m c_{lm}{}^{\alpha*} Y_{lm}(\theta_j,\varphi_j)^*$$
$$\times \sum_{m'} c_{lm'}{}^\alpha Y_{lm'}(\theta_i,\varphi_i). \quad (A6)$$

[17] The tight-binding method has been found to predict exciton absorption at 9 ± 1 ev in solid argon (reference 3). However, it is not known whether the overlap expansions used in this calculation are convergent.
[18] D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936).
[19] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).
[20] H. Kawamura, J. Phys. Chem. Solids **5**, 256 (1958).
[21] K. B. Tolpygo and O. F. Tomasevich, Soviet Phys. (Solid State) **2**, 2765 (1961).

We can formally add to this expression all analogous terms arising from the other symmetrized valence wave functions $\psi_{nl}{}^\beta$ with $\beta \neq \alpha$ since their cross product with $S_i{}^\alpha$ is zero, and then because of the unitary property of the transformation on the Y_{lm}'s this last equation can be written

$$(S_q{}^\alpha, \psi_{nl}{}^\alpha)(\psi_{nl}{}^\alpha, S_p{}^\alpha)$$
$$= [O_{nl}{}^\alpha(\mathbf{k})]^{-1} \sum_i \sum_j a_{qi}{}^{\alpha*} a_{pj}{}^\alpha A_{nl} A_{nl}(|\mathbf{k}+\mathbf{h}_i|)^*$$
$$\times A_{nl}(|\mathbf{k}+\mathbf{h}_j|)[4\pi/(2l+1)]$$
$$\times \sum_m Y_{lm}(\theta_j, \varphi_j)^* Y_{lm}(\theta_i, \varphi_i). \quad (A7)$$

From the addition theorem of spherical harmonics this becomes

$$(S_q{}^\alpha, \psi_{nl}{}^\alpha)(\psi_{nl}{}^\alpha, S_p{}^\alpha)$$
$$= [O_{nl}{}^\alpha(\mathbf{k})]^{-1} \sum_i \sum_j a_{qi}{}^{\alpha*} a_{pj}{}^\alpha$$
$$+ A_{nl}(|\mathbf{k}+\mathbf{h}_i|)^* A_{nl}(|\mathbf{k}+\mathbf{h}_j|)P_l(\cos\omega). \quad (A8)$$

In (A8) ω is the angle between $\mathbf{k}+\mathbf{h}_i$ and $\mathbf{k}+\mathbf{h}_j$.

Formula (A8) has been given by Herring for the particular case of nonoverlapping core states $[O(\mathbf{k})=1]$.

The present derivation makes use of the symmetry of the lattice from the beginning and allows one to treat orthogonalization to valence states in the same way as orthogonalization to nonoverlapping core states. This procedure can be made more general to include the case of mixing of wave functions with different angular quantum numbers in the valence states.

A Magneto-Stark Effect and Exciton Motion in CdS*

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Exciton absorption occurs, for weak exciton lines, at an energy which is the energy of an exciton having a wave vector equal to that of the light in the medium. These excitons have a finite wave vector, and therefore, a finite velocity. In a uniform magnetic field, the Lorentz force on the electron and hole due to the center-of-mass velocity produces a magnetic perturbation in addition to those ordinarily considered. The measurement of such a perturbation measures the velocity of an exciton of known wave vector, and therefore determines the total exciton mass. In addition, the measurement of this effect which depends on the exciton velocity provides a positive distinction between exciton absorption lines and absorption lines due to impurities. It is shown that this perturbation can be measured by the measurement of the Stark effect on excitons in the presence of a uniform magnetic field. The exciton mass for the $n=2$ states of excitons formed from the top valence band in CdS was measured by this technique, and found to be 0.92 ± 0.18 in reasonable agreement with the mass calculated from independent experiments. The Stark effect in the absence of a magnetic field was also studied to ensure an understanding of the effect in the presence of a magnetic field. The stark effect in a magnetic field sometimes exhibits peculiar behavior which was attributed to an extraneous Hall field. This interpretation gives an estimate of $\omega_c \tau_r \approx 2$ for electrons in "good" CdS crystals at 1.6°K and at 31 000 gauss.

I. INTRODUCTION

THE optical absorption of insulating crystals having a direct band gap is often dominated, at energies near the band gap, by the absorption due to excitons. These bound electron-hole pairs cause a series of discrete absorption lines below the band gap. Many experiments have been performed to try to demonstrate exciton motion or the current-free transport of energy by excitons. These experiments have, by and large, been marginal and ambiguous.

Recent work by Hopfield and Thomas[1,2] in CdS and by Gross[3] in Cu_2O has shown that the finite wave vector of light having band-gap energies can produce easily observed effects on the selection rules for exciton transitions. Although both experiments could be most easily interpreted on the basis of exciton states, the finite wave vector of the light can produce similar effects on the absorption due to impurity atoms.

The present experiments describe the measurement of the *velocity* $\mathbf{v}$ of an exciton of known wave vector. The possibility of such experiments[1] and early experimental work[4,5] has been previously reported. The experiments

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