Energy Bands for Solid Argon*

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Energy bands have been calculated for solid argon using the augmented plane-wave method. The crystal potential used in this calculation has been approximated by a superposition of atomic potentials and involves the Slater free-electron exchange approximation. In order to estimate the error introduced by this approximation, a quantitative comparison has been made between the Hartree-Fock and free-electron exchange potentials for atomic argon. The results indicate that the free-electron exchange approximation is most accurate for the less tightly bound valence electrons, though errors of the order of 0.1 Ry remain. The present energy bands are found to be in qualitative agreement with the earlier results of Knox and Bassani, though there are important quantitative differences. The present calculation yields a band gap of 13.3 eV, which is in fair agreement with the experimentally observed value of 14.3 eV.

I. INTRODUCTION

THE energy bands for solid argon have been calculated recently by Knox and Bassani[1] using a perturbation approximation to the orthogonalized-plane-wave (OPW) method developed by Bassani and Celli.[2] The 3s and 3p levels were calculated using the tight binding approximation, and the OPW method was modified to take into account the variation of these core levels with wave vector. It seemed desirable to carry out a similar calculation using the augmented-plane-wave (APW) method[3,4] in order to determine whether or not this method was practical when narrow valence bands and nearly free-electron conduction bands were involved.

It turns out that the APW method is capable of handling without difficulty both the tightly bound valence band and the excited conduction band states. The general features of the 3s and 3p valence bands obtained by the APW method are very similar to those calculated by Knox and Bassani using the tight binding approximation. However, the corresponding positions of these bands on an absolute energy scale (relative to electron at rest at infinity) differ significantly in the two calculations. In the case of the conduction bands, there are again differences in the absolute energies of the various states, but more important, there are differences in the relative ordering of states. These discrepancies cannot be attributed to a difference in potential since checks were made with the same potential which was used by Knox and Bassani, and similar differences were obtained.

The general method for constructing the crystal potential which has been used in the present calculation is described in Sec. II. Exchange has been introduced by means of Slater's free-electron exchange approximation.[5]

Section III contains a quantitative discussion of this approximation in its application to the argon atom. It is found that the free-electron exchange approximation does not always overestimate exchange, as is frequently emphasized in the literature.[6,7] It is shown that the changes in the one-electron energies of the various electrons in going from the Hartree-Fock to the free-electron exchange approximation can be estimated quite accurately by means of first-order perturbation theory. This provides one with a reasonable estimate of the accuracy with which a given potential will represent the relative positions of the different bands on an absolute energy scale, at least in the case of narrow non-overlapping bands. This information is particularly important in the vicinity of the Fermi surface and in the interpretation of such phenomena as optical absorption. The results of the present APW calculations for solid argon are presented in Sec. IV, while Sec. V contains a brief discussion of these results and the accuracy of the free-electron exchange approximation.

II. CRYSTAL POTENTIAL

Solid argon is face-centered cubic, with a lattice constant of 10.03 au (5.31 Å).[8] In the APW method, the crystal potential is usually approximated by a so-called "muffin-tin" potential. Each atom is surrounded by a sphere, inside of which the potential is spherically symmetric. Between spheres, the potential is assumed to be constant. This constant is usually chosen to be the average value of the potential in the region between the sphere and the boundaries of the Wigner-Seitz cell. In the present calculation, the radius of the inscribed sphere was chosen so that the spheres surrounding neighboring atoms just touched at the cell boundaries.

The crystal potential for solid argon has been approximated by a superposition of spherically sym-

¹ R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).
² F. Bassani and V. Celli, Phys. Chem. Solids **20**, 64 (1961).
³ J. C. Slater, Phys. Rev. **51**, 846 (1937).
⁴ J. H. Wood, Phys. Rev. **126**, 517 (1962).
⁵ J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960).

⁶ J. Callaway, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 100.
⁷ J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters **9**, 215 (1962).
⁸ E. R. Dobbs and G. O. Jones, in *Reports on Progress in Physics*, edited by A. C. Stickland (The Physical Society, London, 1957), Vol. 20, p. 516.

TABLE I. The crystal potential for face-centered cubic argon. The radial distance r is in atomic units and $V(r)$ is in rydbergs. The average potential in the region between the APW sphere and the Wigner-Seitz cell is -0.3697 rydberg.

r	$-V(r)$	r	$-V(r)$
0.01	3502.9162	0.46	29.9888
0.02	1701.5038	0.50	26.0148
0.03	1101.5748	0.54	22.7465
0.04	802.5071	0.58	20.0256
0.05	623.9115	0.62	17.7405
0.06	505.5518	0.66	15.8101
0.07	421.5774	0.70	14.1721
0.08	359.0582	0.80	11.0417
0.09	310.8172	0.90	8.8422
0.10	272.5569	1.00	7.2112
0.12	215.9745	1.10	5.9544
0.14	176.4496	1.20	4.9645
0.16	147.5126	1.30	4.1747
0.18	125.5360	1.40	3.5391
0.20	108.3462	1.50	3.0238
0.22	94.5796	1.60	2.6030
0.24	83.3456	1.70	2.2569
0.26	74.0382	1.80	1.9701
0.28	66.2300	1.90	1.7307
0.30	59.6094	2.00	1.5291
0.34	49.0545	2.50	0.8828
0.38	41.0828	3.00	0.5568
0.42	34.8983	3.50	0.3966

metric atomic potentials, calculated from self-consistent field Hartree-Fock solutions for the argon atom by Watson and Freeman.[9] Exchange has been treated by means of Slater's free-electron exchange approximation. In discussing the manner in which the crystal potential has been approximated, it is convenient to consider the Coulomb and exchange contributions separately.

The total Coulomb potential at a given lattice site (which is taken to be at the origin of coordinates) has been represented by the neutral atom Coulomb potential for argon, plus contributions from neighboring Coulomb potentials. The effects of neighboring Coulomb potentials have been introduced by expanding them about the origin, using Löwdin's alpha-function expansion.[10] To obtain a spherically symmetric crystal Coulomb potential, it is necessary to include only the $l=0$ term from this expansion in spherical harmonics. In the case of argon, the large lattice spacing required only the inclusion of the effects from nearest-neighboring Coulomb potentials.

An analogous method has been used to calculate an approximation to the crystal exchange potential. According to Slater's free-electron exchange approximation,[5]

$$V^{fe}(\mathbf{r}) = -6[3\rho(\mathbf{r})/8\pi]^{1/3}. \tag{1}$$

In the atomic case, $\rho(\mathbf{r})$ represents the charge density of the occupied states. We have approximated the crystal charge density by a superposition of atomic charge densities, again using Löwdin's alpha-function

expansion, and again keeping only the spherically symmetric terms. Then, Eq. (1) was applied, using for $\rho(\mathbf{r})$, the total charge density. As before, the large lattice spacing for argon required only the effects of nearest neighbors to be included in this calculation.

Clearly, such methods for constructing the Coulomb and exchange potentials are not too important in argon, where the occupied atomic functions are well localized and neither the Coulomb potentials nor the charge densities overlap appreciably. However, this approach has been found to yield reasonable results when applied to the elements of the iron-transition series, which follow argon in the periodic table. The crystal potential for argon used in the present calculations is tabulated in Table I. This potential differs only slightly from the corresponding atomic potential, the largest difference being approximately 0.04 Ry near the APW sphere radius.

In view of the statements that the free-electron exchange approximation overestimates the exchange effect, especially in the low-density tails of atomic functions,[7] it seems worthwhile to examine this situation in more detail here. If this were the case, the method for constructing the exchange potential which is described here would only exaggerate this effect. The results of such an investigation are presented in Sec. III.

III. COMPARISON OF HARTREE-FOCK AND FREE-ELECTRON EXCHANGE POTENTIALS

A comparison of the Hartree-Fock and various approximate averaged exchange potentials for an atomic system has been carried out previously by Herman, Callaway, and Acton for germanium.[11] Since they used self-consistent field solutions for germanium computed without exchange, it was felt that some of their results might be misleading due to inaccurate wave functions. We shall make a similar comparison for the argon atom using accurate solutions to the Hartree-Fock equations. We shall limit this discussion to a comparison of the Hartree-Fock and free-electron exchange potentials.

For an atom with closed shells, the Hartree-Fock exchange potential for an electron in a state with quantum numbers n, l can be written:

$$V_{nl}^{HF}(r) = -\left[\sum_{n'l'} \sum_{k} c^k(l0; l'0) \right.$$

$$\left. \times \left(\frac{2l'+1}{2l+1}\right)^{1/2} \frac{P_{n'l'}(r)}{P_{nl}(r)} \frac{2}{r} Y_k(n'l', nl|r) \right]. \tag{2}$$

The sum is over all closed shells of the atom, the coefficients $c^k(l0; l'0)$ are tabulated integrals over spherical harmonics, the functions $P_{nl}(r)$ are the radial wave

[9] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 (1961).
[10] P. O. Löwdin, Advan. Phys. 5, 1 (1956).

[11] F. Herman, J. Callaway, and F. S. Acton, Phys. Rev. 95, 371 (1954).

TABLE II. A comparison of $P_{nl}^2(r) V_{nl}^{HF}(r)$ and $P_{nl}^2(r)^{fe}(r)$ as a function of r for atomic argon. r is in atomic units.

r	$-P_{1s}^2 V_{1s}^{HF}$	$-P_{1s}^2 V^{fe}$	$-P_{2s}^2 V_{2s}^{HF}$	$-P_{2s}^2 V^{fe}$	$-P_{3s}^2 V_{3s}^{HF}$	$-P_{3s}^2 V^{fe}$	$-P_{2p}^2 V_{2p}^{HF}$	$-P_{2p}^2 V^{fe}$	$-P_{3p}^2 V_{3p}^{HF}$	$-P_{3p}^2 V^{fe}$
0.02	150.290	157.508	9.120	12.310	0.819	1.199	0.088	0.134	0.0064	0.0108
0.04	258.737	243.887	13.915	17.009	1.226	1.639	0.802	1.205	0.065	0.095
0.06	246.303	214.555	10.421	11.678	0.892	1.096	2.351	3.466	0.158	0.270
0.08	186.170	151.636	4.941	4.993	0.404	0.440	4.474	6.340	0.288	0.485
0.10	125.757	96.795	1.161	0.992	0.085	0.070	6.908	9.221	0.423	0.691
0.20	10.991	7.785	11.316	10.597	0.857	1.099	18.645	19.986	0.910	1.277
0.40	0.0922	0.0254	18.028	14.855	0.540	0.531	13.384	12.015	1.957	1.860
0.60	0.0015	0.00009	4.782	3.280	0.085	0.174	3.385	2.572	0.078	0.172
0.80			0.876	0.568	1.010	1.031	0.669	0.494	0.606	0.719
1.00			0.152	0.103	1.780	1.666	0.128	0.103	1.088	1.179
1.40			0.0059	0.0027	1.639	1.378	0.0057	0.0037	1.193	1.189
1.80			0.00041	0.00008	0.821	0.600	0.00041	0.00015	0.744	0.679
2.20					0.324	0.202			0.365	0.304
2.60					0.115	0.060			0.165	0.120
3.00					0.040	0.017			0.070	0.045

functions, and $Y_k(n'l',nl/r)$ represent the functions

$$Y_k(n'l', nl|r) = \frac{1}{r^k} \int_0^r P_{n'l'}(r') P_{nl}(r') r'^k dr'$$

$$+ r^{k+1} \int_r^\infty \frac{P_{n'l'}(r') P_{nl}(r')}{r'^{k+1}} dr'. \quad (3)$$

For purposes of comparing the Hartree-Fock and free-electron exchange potentials, it is convenient to calculate $P_{nl}^2(r) V_{nl}^{HF}(r)$ and $P_{nl}^2(r) V^{fe}(r)$. The results of such calculations for atomic argon are given in Table II. From these results, it is clear that the free-electron exchange approximation *underestimates* exchange at large values of the radial distance r for all occupied atomic states. An earlier calculation by Hartree[12] on Cu+ produced similar results. Hartree plotted the various Hartree-Fock exchange potentials as a function of the radial distance r. According to his figures, the free-electron exchange approximation underestimates exchange for all occupied states at a radial distance of 2 au.

It is interesting to take the difference between the Hartree-Fock and free-electron exchange potentials, use this as a perturbation, and apply first-order perturbation theory to determine the first-order corrections to the one-electron energy levels. This involves either the evaluation of the $F^k(nl; n'l')$ and $G^k(nl; n'l')$ integrals,[5]

in addition to the integrals

$$\int_0^\infty P_{nl}^2(r) V^{fe}(r) dr, \quad (4)$$

or the direct integration of the differences between $P_{nl}^2(r) V_{nl}^{HF}(r)$ and $P_{nl}^2(r) V^{fe}(r)$. The results of such calculations for argon are given in Table III.

A good estimate of the accuracy of using perturbation theory can be obtained by direct integration of the radial Schrödinger equation, using the potential obtained from the Hartree-Fock solutions and the free-electron exchange approximation. This would represent the first iteration in going from Hartree-Fock to self-consistent solutions involving the free-electron exchange approximation, usually designated Hartree-Fock-Slater solutions. These energies are also given in Table III. For comparison, the eigenvalues for the self-consistent Hartree-Fock-Slater solutions, as obtained by Herman and Skillman,[13] are also included. The differences between the Hartree-Fock eigenvalues and those obtained from the first iteration compare well with the perturbation theory results. Comparison with the Hartree-Fock-Slater eigenvalues indicates that there are still significant adjustments in the eigenvalues before self-consistency is achieved, though these changes are not large for the less tightly bound electrons.

TABLE III. The eigenvalues $\epsilon_{nl}^{(a)}$ and $\epsilon_{nl}^{(c)}$ are the self-consistent Hartree-Fock and Hartree-Fock-Slater one-electron energies, respectively, for atomic argon (in Ry). The energies $\epsilon_{nl}^{(b)}$ represent eigenvalues for the radial Schrödinger equation involving a potential computed from the Hartree-Fock charge density and the free-electron exchange approximation.

nl	$\epsilon_{nl}^{(a)}$	$\epsilon_{nl}^{(b)}$	$\epsilon_{nl}^{(c)}$	$\epsilon_{nl}^{(b)} - \epsilon_{nl}^{(a)}$	$\int_0^\infty P_{nl}^2[V^{fe} - V^{HF}] dr$
1s	−237.21	−234.15	−232.44	3.06	3.19
2s	−24.64	−23.55	−22.79	1.09	1.01
2p	−19.14	−19.04	−18.13	0.10	0.12
3s	−2.55	−2.34	−2.05	0.21	0.23
3p	−1.18	−1.25	−1.01	−0.07	−0.05

[12] D. R. Hartree, Phys. Rev. 109, 840 (1958).
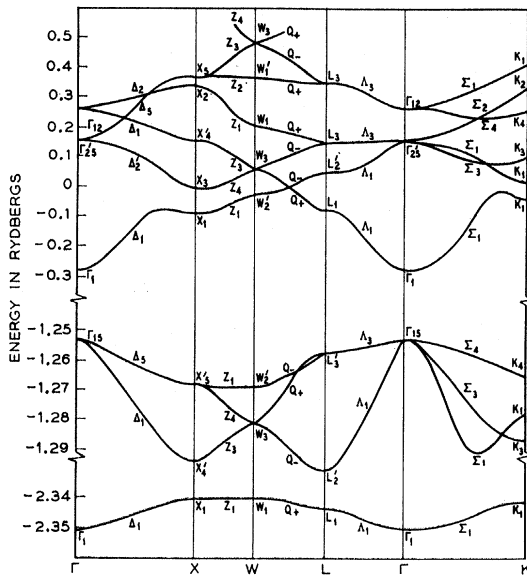[13] F. Herman (private communication).

FIG. 1. Energy bands for face-centered cubic argon. Calculations were carried out only at the points Γ, X, W, L, and K of the Brillouin zone. The connecting lines represent reasonable guesses to the actual shapes of the bands. Energies are given in Ry. Note the change in scale between the valence $3s$ and $3p$ bands and the conduction bands.

The results of Table III indicate that the free-electron exchange potential, averaged over all r, underestimates exchange for the $1s$, $2s$, and $2p$ levels, and overestimates it slightly for the $3p$ level. However, the $3p$ eigenvalue also rises above the Hartree-Fock value by the time self-consistency is achieved.

IV. RESULTS

The results of the APW calculations for solid argon are listed in Table IV and sketched in Fig. 1. Convergence tests indicate that these results are accurate to approximately 0.001 Ry for the potential under consideration. Actual calculations have been carried out only at the points Γ, X, W, L, and K in Brillouin zone. The notation is that of Bouckaert, Smoluchowski, and Wigner.[14] The lines connecting these points represent reasonable guesses to the actual shapes of the various bands, consistent with the compatibility relations.

The calculated widths of the $3s$ and $3p$ valence bands compare favorably with those reported earlier by Knox and Bassani.[1] However, the present bands are located at higher energies. From the results of Table III, it is seen that the present $3s$ and $3p$ bands lie in the immediate vicinity of the corresponding atomic levels obtained from the free-electron exchange calculations.

The APW results for the conduction bands differ significantly from those of Knox and Bassani. The two calculations agree only in predicting that the bottom of

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

the conduction band lies at Γ, and has the symmetry Γ_1. The APW results indicate that the $3d$ band lies in the middle of the $4s$–$4p$ conduction band, and that the lowest states at the edges of the Brillouin zone are predominantly "d" like rather than "s" or "p" like, as predicted by Knox and Bassani. Again, the energy range of the conduction bands differs considerably from that of Knox and Bassani.

V. DISCUSSION

The present calculations predict an energy gap of 13.3 eV from the top of the $3p$ valence band (Γ_{15}) to the bottom of the conduction band (Γ_1). This value compares well with the experimental value of 14.3 eV measured by Baldini,[15] and the value of 12.4 eV obtained in the calculations by Knox and Bassani.

These results indicate that quite reasonable energy bands can be obtained using the free-electron exchange approximation. Despite the fact that this approximation causes changes in the one-electron atomic energy levels from the Hartree-Fock values (and a corresponding shift in the energies of the resultant bands), it appears likely that this shift in energy can be estimated reasonably well by first-order perturbation theory. This will give at least a rough estimate of the inaccuracy in the relative positions of the different bands.

The source of the discrepancies between the present results and the earlier calculations by Knox and Bassani is uncertain. The fact that their $3s$ and $3p$ bands are lower in energy is probably due to the fact that they used the Hartree-Fock eigenvalues to position these

TABLE IV. Energies of various states for solid argon at the center and boundaries of the first Brillouin zone. All values are in Ry and are relative to zero potential in the vacuum outside the boundaries of the crystal.

State	$3s$ band	$3p$ band	Conduction bands		
Γ_1	−2.351		−0.274		
$\Gamma_{25'}$			0.158		
Γ_{12}			0.265		
Γ_{15}		−1.253	1.439		
X_1	−2.341		−0.085	0.603	0.881
X_2			0.339		
X_3			−0.002		
$X_{4'}$		−1.294	0.157		
X_5			0.367		
$X_{5'}$		−1.268	0.530	1.582	
W_1	−2.341		0.204	0.518	
$W_{1'}$			0.364		
$W_{2'}$		−1.269	−0.028	0.620	1.126
W_3		−1.281	0.058	0.481	1.052
L_1	−2.344		−0.077	0.503	
$L_{2'}$		−1.297	0.044		
L_3			0.144	0.345	
$L_{3'}$		−1.258	1.517		
K_1	−2.342	−1.278	−0.038	0.014	0.410
K_2			0.334		
K_3		−1.287	0.101	0.470	
K_4		−1.265	0.256	0.683	1.573

[15] G. Baldini, Phys. Rev. 128, 1562 (1962).

bands. This may also have produced the differences in the ordering of the conduction band states. These latter differences could also be due to limitations in the perturbation approximation to the orthogonalized-plane-wave method which was used by Knox and Bassani.

One interesting observation regarding the conduction bands for argon is the similarity between these bands and those obtained for face-centered cubic iron by Wood[4] and for copper by Burdick[16] and also by Segall.[17] Aside from minor changes in the ordering of states in the $4s-4p$ bands (which can be explained by differences in lattice spacing), the bands are remarkably similar. This

may lend some support to the rigid band approximation, a proposal which has enjoyed fair success in explaining several aspects of the electronic properties of the transition metals and their alloys.

VI. ACKNOWLEDGMENTS

[16] G. A. Burdick, Phys. Rev. 129, 138 (1963).
[17] B. Segall, Phys. Rev. 125, 109 (1962).

Second-Sound Propagation in Dielectric Solids*

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The conditions necessary for the occurrence of second sound in solids are examined in some generality. The results indicate that second sound can propagate at frequencies greater than the reciprocal umklapp relaxation time and smaller than the reciprocal normal relaxation time. At frequencies less than the reciprocal umklapp relaxation time, the solutions are the same as those for normal thermal conductivity. The frequency range and damping of second sound at various temperatures is computed using relaxation times determined for sodium fluoride.

I. INTRODUCTION

SECOND sound in superfluid helium was first described as a collective phonon wave by Landau.[1] In this description, the "phonon gas" was treated as a particle gas in which harmonic phonon-density fluctuations could be propagated. This explanation seemed to describe a phenomenon so general that many authors[2] have speculated about the possibility of occurrence of similar collective waves in solids. A collective wave of a more restricted nature has been reported in CdS crystals by Kroger, Prohofsky, and Damon.[3] Their experiment involved the use of electrons drifting faster than the velocity of sound, which are therefore strongly coupled to the phonons. This problem will be discussed in a forthcoming paper.

This paper is limited (as were those by Ward and Wilks, and by Dingle[2]) to a discussion of an acoustic

phonon system which does not interact strongy with charged particles or optical phonons. We will place emphasis on those aspects of phonon dynamics associated with the periodic structure of solids. This requires that a distinction be made between normal collisions and umklapp collisions. It should be kept in mind that phonons undergo normal collisions in which the crystal momentum of all the phonons is conserved, much like the collisions of a particle gas. It is emphasized that this conservation applies regardless of the number of phonons or whether the collision involves phonons of the same or different phonon branches. The major difference between phonon and particle gases is that in addition to normal collisions the phonons may undergo umklapp collisions which have no counterpart in particle gases. In this context this paper examines in detail the collective transport phenomena of a many-phonon system and develops a description of a collective harmonic mode.

In Sec. II of this paper, the factors that determine whether or not a system will respond to a density fluctuation by diffusive or harmonic behavior are discussed qualitatively.

In Sec. III, energy and crystal-momentum conservation equations for phonons are derived from transport equations. The moments of the equations are then

[1] L. D. Landau, J. Phys. Moscow 5, 71 (1941), 11, 91 (1947).
[2] (a) J. C. Ward and J. Wilks, Phil. Mag. 42, 314 (1951), 43, 48 (1952). (b) R. B. Dingle, Proc. Phys. Soc. (London) A65, 374 (1952). (c) M. Chester, Phys. Rev. 131, 2013 (1963).
[3] H. Kroger, E. W. Prohofsky, and R. W. Damon, Phys. Rev. Letters 11, 246 (1963).