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PHYSICAL REVIEW B VOLUME 8, NUMBER 2 15 JULY 1973

Study of the Electronic Structure and the Optical Properties of the Solid Rare Gases*

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(Received 22 January 1973)

In this paper, we present a series of band-structure calculations for solid Ne, Ar, and Kr. These calculations are performed in the restricted Hartree-Fock limit by the self-consistent-field method. Correlation and polarization corrections are included by means of the electronic polaron model. We find that the Hartree-Fock band structures provide band structures which are broader than one obtains using a statistical-exchange approximation in constructing a crystal potential. We find that correlation corrections produce optical band gaps in reasonable agreement with experiment. We compute the joint density of states for optical transitions from both valence and core levels and find acceptable agreement with experiment. We also study the mixed-crystal soft-x-ray data of Haensel *et al*. and find our band structures to be in reasonable agreement with the trends demonstrated in the experimental data. This is in contrast to the other available unified series of calculations for the solid rare gases of Rössler. In this other series of calculations employing a statistical-exchange approximation, one finds that the shift in conduction levels in going from solid Kr to solid Ar to be opposite to experiment.

I. INTRODUCTION

The solid rare gases have been studied in a number of band-structure calculations. The available calculations have been performed either using a statistical-exchange approximation in forming the crystal potential or in the restricted Hartree-Fock limit. In general, great differences are found to exist between these two types of calculations. In the present paper, we present a set of fully self-consistent Hartree-Fock band-structure calculations for solid Ne, Ar, and Kr. We also include polarization and correlation corrections to these band structures. We compute our band structure at a sufficiently large number of points throughout the first Brillouin zone to permit us to compute density of states and the joint density of states for our solids without the need of interpolation schemes.

Previously, Knox and Bassani[1] have computed the band structure of solid Ar using a perturbation approach to the orthogonalized-plane-wave (OPW) method. Mattheiss[2] has later computed the band structure of solid Ar using the augmented-plane-wave (APW) method. Most recently Rössler[3] has computed a band structure for solid Ar using the Korringa-Kohn-Rostoker (KKR) method. In the case of solid Kr, there exists a combined tight-binding-OPW calculation by Fowler[4] and a KKR calculation by Rössler.[3] Finally in the case of solid Ne there exists a calculation by Rössler.[3] All of these calculations employ a statistical-exchange approximation in forming the crystal potential and none of them is self-consistent.

More recently, physicists have been attempting to employ the restricted Hartree-Fock method to study these materials. Calculations of this nature have been reported for solid Ne using the APW method by Dagens and Perrot.[5] Calculations for solid Ar have been reported by Lipari and Fowler[6] who used the OPW method and by Lipari[7] using the mixed-basis (MB) method, and by Dagens and

Perrot[5] using the APW method. Lipari[8] has reported a calculation for solid Kr employing the OPW method. Most recently Mickish and Kunz[9] have reported a calculation for solid Ar obtained using the linear-combination-of-local-basis-functions (LCLBF) method.[10] Of these Hartree–Fock calculations only the calculation of Lipari for solid Ar and the calculation of Mickish and Kunz for solid Ar have been self-consistent. The only calculation to report a band structure which specifically included correlation corrections was that of Lipari and Fowler for solid Ar. This calculation, unfortunately, was not self-consistent.

We report in this paper a series of self-consistent calculations for solid Ne, Ar, and Kr. These calculations are performed in the self-consistent Hartree–Fock approximation using the LCLBF band method.[10] Self-consistency is achieved by solving the Adams–Gilbert[11,12] local-orbitals equation in the limit of small overlap.[13] We include polarization and correlation corrections in these calculations. We do this using the electronic polaron method of Toyozawa[14] for both the electrons and the holes in the limit recently derived by Kunz.[15] We find these corrections to be substantial and important, as previously suggested by Fowler[16] and as found by Lipari and Fowler.[6]

At this point some immediate observations are possible. These are that there exists an acceptable level of agreement as to the band structure of the solid rare gases in the calculations which employ a statistical-exchange approximation and also an acceptable level of agreement as to the band structure of the solid rare gases in the Hartree–Fock-type calculations. What is also evident is that there exists gross disagreement between the predictions obtained using a statistical-exchange approximation and those obtained using a Hartree–Fock method. This statement is not to imply that the agreement among the various calculations of a given type is perfect but rather that such disagreements as exist are minor by comparison with the disagreement which exists between Hartree–Fock and statistical-exchange calculations. We note that these differences continue to exist even after self-consistency is imposed upon the Hartree–Fock solution and after polarization and correlation corrections are included.

In the comparisons which follow in this paper, the statistical-exchange calculations we will use for comparison purposes are those of Rössler.[3] This is because these calculations are the most recent and the most complete. That is, the calculations of Rössler are for solid Ne, Ar, Kr, and Xe and employ a similar type of potential and employ the same band model for all calculations. Therefore the trends from one material to the next should accurately represent the physics of the situation and should not be limited by minor differences in potential or band model as would be the case if we used the calculations of several authors as a standard of comparison. In addition, Rössler has attempted detailed experimental comparisons from his calculations[17] and also detailed comparisons with other theoretical results.[18] We find that a substantial error has been made in Rössler's comparison of his calculation[3] with that of Lipari.[8] We investigate this question at the proper place in this paper.

Owing to the efficiencies possible in the LCLBF band model we compute our band structures for the solid rare gases at sufficient points in the Brillouin zone to permit us to construct coarse but reasonable density-of-state histograms directly from our band model without the aid of interpolation schemes. We also compute the joint density of states for transitions from the valence levels and for certain of the core levels for the solid rare gases. This facilitates comparison of theory and experiment.

The experimental situation for the solid rare gases is excellent. Optical absorption or reflection studies have been performed and electron-energy-loss data in the region of the fundamental exciton absorption and the valence-to-conduction band-to-band region have been determined.[19–22] In addition there have been a series of studies of the optical properties of the solid rare gases in the soft-x-ray region. Solid Ne has been studied in the region of the $L_{\rm I}$ edge by Haensel *et al.*[23] Solid Ar has been studied in the region of the $L_{\rm II,III}$ edge by Haensel *et al.*[24] and by Keitel.[25] Solid Kr has been studied in the $M_{\rm IV,V}$ edge region by Schreiber[26] and by Haensel *et al.*[27] Finally the optical properties of alloys of Ne-Ar have been studied in the region of the Ne $L_{\rm I}$ edge, and of Ar-Kr in the region of the Kr $M_{\rm IV,V}$ edge, by Haensel *et al.*[28] In this paper we attempt detailed comparison of our calculation with the results of these experiments.

In Sec. II we briefly discuss the method of calculation employed for obtaining the band structure and also the polarization-correlation corrections. In Sec. III we compare our results with those of other calculations. In Sec. IV the predictions of these and other calculations are compared with experiment. Finally in Sec. V we discuss the total situation and draw conclusions.

II. DETAILS OF THE CALCULATION

The authors have already expounded upon the method of calculation employed in these studies elsewhere[9]; therefore we only give a condensed outline of our methods in this section. We employ the LCLBF method. This method is essentially a generalization of the linear-combinations-of-atomic-orbitals (LCAO) method[29] or the MB method.[30] The basis set employed here consists of self-consistent local orbitals for all the occupied levels and of Slater-type orbitals (STO's) to describe the virtual or conduction levels. A method similar to this has been employed with good success for diamond.[10]

The Fock operator is a functional of the first-order density matrix $\rho(\vec{r}, \vec{r}')$. Thus we have that

$$F = -\nabla^2 - \sum_I \frac{2Z_I}{|\vec{r} - \vec{R}_I|} + 2\int \frac{\rho(\vec{r}', \vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}' - \frac{2\rho(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \tag{1}$$

with

$$\rho(\vec{r}, \vec{r}') = \sum_{Ai} \sum_{Bj} \xi_{Ai}(\vec{r} - \vec{R}_A) S^{-1}_{Ai,Bj}\, \xi^{\dagger}_{Bj}(\vec{r}' - \vec{R}_B), \tag{2}$$

$$S_{Ai,Bj} = \int \xi_{Ai}(\vec{r} - \vec{R}_A)\, \xi^{*}_{Bj}(\vec{r} - \vec{R}_B)\, d\vec{r}, \tag{3}$$

and

$$[F - \rho A_A \rho]\, \xi_{Ai}(\vec{r} - \vec{R}_A) = E_{Ai}\, \xi_{Ai}(\vec{r} - \mathrm{R}_A). \tag{4}$$

Here we employ the rydberg as the unit of energy, $e = \sqrt{2}$, $m = 0.5$, $\hbar = 1$. We employ upper-case letters to denote nuclear properties and coordinates and lower-case letters to denote electron properties and coordinates. Equation (4) is the Adams–Gilbert local-orbitals equation and the operator A_A contained in it may be any Hermitian operator.[11,12]

In the limit of small overlap, such as is appropriate for the solid rare gases,[31] the ξ_{Ai} satisfy the equation (letting $A_A = U_A$)

$$[F_A + U_A - E_{Ai}]\, \xi_{Ai} = \sum_j \sum_k \xi_{Aj} \langle Aj | U_A | Ak \rangle \langle Ak | Ai \rangle, \tag{5}$$

where

$$F_A = -\nabla^2 - \frac{2Z_A}{|\vec{r} - \vec{R}_A|} + 2\int \frac{\rho_A(\vec{r}', \vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}' - \frac{2\rho_A(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}, \tag{6}$$

$$U_A = \sum_{B \neq A} \left[\frac{-2Z_B}{|\vec{r} - \vec{R}_B|} + 2\int \frac{\rho_B(\vec{r}', \vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}' \right], \tag{7}$$

and

$$\rho_C(\vec{r}, \vec{r}') = \sum_i \xi_{Ci}(\vec{r})\, \xi^{\dagger}_{Ci}(\vec{r}') . \tag{8}$$

We solve the system of equations (5)–(8) self-consistently using an analytic expansion technique in terms of STO's.[32] We have previously reported such self-consistent local orbitals for solid Ne[33] and solid Ar.[34] It is these local orbitals which we employ in this calculation. We note that in a recent calculation for solid Ar, Lipari also used these same local orbitals. In the case of Ne and Ar we employed a basis set obtained by Bagus.[35] In the case of solid Kr, there have been no self-consistent local orbitals reported. Therefore we have computed the self-consistent local orbitals for solid Kr using a basis developed for the Kr atom by Watson and Freeman.[36] We present the local orbitals and their basis for solid Kr in Table I.

Once we have obtained the local orbitals, we form the Fock operator according to Eqs. (1)–(3). We then form a basis for the band calculation from Bloch-type sums of local orbitals and from Bloch-type sums of STO's. Thus our basis set is comprised of the functions

$$\phi_i = \sum_A \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_A}\, \xi_{Ai}(\vec{r} - \mathrm{R}_A) \tag{9}$$

and

$$\eta_{nlm} = \sum_A \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_A} |\vec{r} - \vec{R}_A|^{n+l-1} \times y_l^m(\vec{r} - \vec{R}_A) e^{-\alpha_{nl}|\vec{r} - \vec{R}_A|} . \tag{10}$$

Therefore, using this basis and the previously obtained Fock operator one must evaluate matrix elements of the Fock and overlap matrix with respect to such a basis. Thus we need to find three types of integrals,

$$A = \int \phi_i^* O_p \phi_j \, d\tau , \tag{11}$$

$$B = \int \phi_i^* O_p \eta_{nlm} \, d\tau , \tag{12}$$

or

$$C = \int \eta^*_{mln} O_p \eta_{n'l'm'} \, d\tau . \tag{13}$$

Here O_p is either the unit operator or the Fock operator, Eq. (1). In general we either evaluate these matrix elements exactly, approximately, or set them to zero depending on their size and importance. We have discussed this question in great detail elsewhere.[9] Basically, we consider the Fock operator and its matrix elements to a higher degree of accuracy than either Dagens and Perrot,[5] or Lipari,[7] or Lipari and Fowler.[6] That is, Dagens and Perrot terminate atomic Fock operators in such a way so they are nonoverlapping in the crystal. Lipari and Lipari and Fowler permit their atomiclike Fock operators to overlap but do not correct for this overlap. Essentially, we permit our local orbitals which form F to overlap as they should, but we also include corrections implicit in Eq. (2) to correct for this nonorthogonality of the local orbitals. We find, however, that for the rare-gas solids, the approximations of Dagens and Perrot, or Lipari, or Lipari and Fowler are of little or no importance in a practical sense.

Having obtained matrix elements of the Fock and overlap matrix, one obtains the band structure from a simple matrix diagonalization process.

TABLE I. Basis used in computing the Kr local orbitals and the coefficients of these orbitals. The radial part of the local orbital is given by $R_{nl}(r)=\sum_j C_{nlj} N_{lj}\, r^{l+A_{lj}} e^{-Z_{lj} r}$ and $N_{lj}=\{(2Z_{lj})^{2l+3+2A_{lj}}\,[(2l+2A_{lj}+2)!\,]^{-1}\}^{1/2}$. We also give expectation values of the Fock operator F_A+V_A for these local orbitals. These are in rydbergs and are given as $E_{nl,n'l'}$.

Basis (Ref. 36)

	$l=0$		$l=1$		$l=2$	
j	A_{lj}	Z_{lj}	A_{lj}	Z_{lj}	A_{lj}	Z_{lj}
1	0	38.4921	0	24.0396	0	3.2783
2	1	24.1833	0	16.3171	0	5.0929
3	1	17.8567	1	15.4451	0	7.6684
4	2	16.8785	1	10.0129	0	10.5162
5	2	8.7390	1	6.4435	0	16.5546
6	2	6.9088	2	5.6527		
7	3	7.0214	2	3.1628		
8	3	3.8824	2	1.8646		
9	3	2.4802	2	1.3220		
10	3	1.7277				

Matrix Elements

$E_{1s1s}=-1040.43$
$E_{2s2s}=-139.85$
$E_{3s3s}=-21.72$
$E_{4s4s}=-2.32$
$E_{1s2s}=0.0$

$E_{1s3s}=0.0$
$E_{1s4s}=0.0$
$E_{2s3s}=0.0$
$E_{2s4s}=0.0$
$E_{3s4s}=0.0$

$E_{2p2p}=-126.06$
$E_{3p3p}=-16.68$
$E_{4p4p}=-1.06$
$E_{2p3p}=0.0$
$E_{2p4p}=0.0$
$E_{3p4p}=1\times10^{-5}$
$E_{3d3d}=-7.67$

	$l=0$				$l=1$			$l=2$
j	C_{10j}	C_{20j}	C_{30j}	C_{40j}	C_{21j}	C_{31j}	C_{41j}	C_{32j}
1	0.82901	0.28012	0.11263	0.03595	0.11604	0.05063	0.01389	0.09041
2	0.13744	0.17068	0.06638	0.02024	0.71521	0.28401	0.07686	0.46694
3	−0.01998	−0.63656	−0.25086	−0.07662	0.17736	0.17366	0.05178	0.32576
4	0.01773	−0.49541	−0.37998	−0.13864	0.03489	−0.29906	−0.09271	0.18618
5	−0.04617	−0.08127	0.40597	0.26436	−0.00452	−0.79795	−0.25862	0.03209
6	0.07015	0.05415	0.54707	0.00775	0.00139	−0.07075	−0.00155	
7	−0.03304	−0.01207	0.21493	0.23451	0.00001	−0.01914	0.56554	
8	0.00219	−0.00275	0.02719	−0.50984	−0.00007	0.00853	0.47909	
9	−0.00117	0.00196	−0.00875	−0.56718	0.00004	−0.00373	0.08891	
10	0.00041	−0.00075	0.00311	−0.09238				

Note, however, since the $\vec{k}$-dependent phase factors implicit in Eqs. (11)–(13) can be taken out from under the integral sign, the messy integrals which one evaluates in evaluating Eqs. (11)–(13) need only be done for a single point in k space. Thus once one evaluates (11)–(13) the first time, it is a simple and economic matter to evaluate the band structure at a large number of points in the first Brillouin zone. In the calculations reported here, we have evaluated the band structure at 89 nonequivalent points in $\frac{1}{48}$th of the first Brillouin zone. This proved to be sufficient to permit us to evaluate density of states and joint density of states to a sufficient accuracy required for experimental comparisons in the solid rare gases without any need for interpolation schemes. Had it been necessary, we could have evaluated many more points directly.

All the necessary integrals needed to evaluate Eqs. (11)–(13) were evaluated numerically using the Löwdin α-function expansion method.[37] We employ a 30-term expansion in terms of α functions for evaluating our integrals. We find this to be far more than satisfactory, and we have extensively tested this by evaluating known multicenter integrals of all types. In forming the Fock and overlap matrix elements, we include six shells of neighbors about the central site for each integral being evaluated. Thus we include a total of 87 atoms in all when evaluating each term in the Fock or overlap matrix. We have also tested our basis sets for convergence. Needless to say the convergence of the occupied levels (core and valence bands) is essentially perfect. This is as it should be since the local orbitals employed in our basis should be complete on the space of the occupied orbitals. By substantially augmenting our basis set and comparing, we found the occupied levels to be converged to about 0.001 Ry. The virtual orbitals are also well converged but not as well as the occupied orbitals. We find the virtual orbitals in the region from about

TABLE II. The core levels in solid Ne, Ar, and Kr are given. Results are in rydbergs and spin-orbit effects are absent.

Level	Ne	Ar	Kr
1*s*	−65.61	−237.4	−1042
2*s*		−24.66	−139.8
2*p*		−19.14	−126.1
3*s*			−21.72
3*p*			−16.68
3*d*			−7.650

TABLE IV. Energies of points of high symmetry for the argon band structure, with and without correlation. Results are in eV and we employ the notation of Ref. 41.

	Hartree–Fock			With correlation		
Level	1st	2nd	3rd	1st	2nd	3rd
Γ_1	−35.2	2.80		···	1.12	
Γ_{15}	−15.7	33.8		−14.1	32.1	
Γ'_{25}	12.9	32.7		11.2	31.0	
Γ_{12}	15.7	37.8		14.0	36.1	
X_1	−34.6	5.80	32.1	···	4.12	30.4
X'_4	−16.8	10.6		−15.1	8.9	
X'_5	−15.8	18.2		−14.2	16.5	
X_3	8.47	28.9		6.79	27.2	
X_2	17.3			15.6		
X_5	17.8			16.1		
L_1	−34.8	6.57	20.5	···	4.89	18.8
L'_2	−17.0	8.66		−15.3	6.98	
L'_3	−15.6	27.9		−14.1	26.2	
L_3	12.6	17.3		10.9	15.6	

0.0 to 2.0 Ry to be converged to about 0.01 Ry or better. In all but the solid-Ne calculation, we employ a basis consisting of *s*-, *p*- and *d*-type orbitals about each site. In the case of Ne only an *s*, *p* basis was considered. In direct comparison of our results to those of Lipari or Dagens and Perrot, one must remember that these other calculations include also *f*-type orbitals in the basis and thus one should only compare the parts of the band structures arising from *s*, *p*, or *d* levels. This is a point of little practical importance since the *f* levels lie mostly above the conduction levels of experimental interest and also the optical transitions to these lower *f* levels are suppressed by a centrifugal-barrier effect.[38] In principle and in practice we could include *f* levels in our calculation; however, we believe that for all practical purposes, their inclusion is not worth the added cost in computer time.

All these calculations were performed on a Xerox Σ-5 computer using codes written by the authors. This computer is a medium speed, small-memory-type computer, but nonetheless is adequate for band calculations of the complexity described in this paper. In Table II, we give the calculated core levels for solid Ne, Ar, and Kr in the restricted Hartree-Fock approximation. In Table III, we give the energies of selected symmetry levels in the solid-Ne band structures; a similar tabulation is found for solid Ar in Table IV and for solid Kr in Table V. We have computed the effective masses for the valence-band maximum and conduction-band minimum and list them in Table VI for Ne, Ar, and Kr. We show the Hartree–Fock band structure of solid Ne in Fig. 1 as well as the state density. In Fig. 2 we show the Hartree–Fock band structure of solid Ar and the density of states. Finally in Fig. 3 we show the Hartree–Fock band structure and state density for solid Kr.

Having obtained the Hartree–Fock band structure for solid Ne, Ar, and Kr, we desired to include polarization and correlation effects in our calculation. It is possible to include polarization and correlation corrections by a variety of methods. The simplest and most economical method is that due to Fowler.[16] In this method one treats the conduction electron or the valence hole as a point charge, statically situated on a nuclear site. One then

TABLE III. Energies of points of high symmetry for the neon band structure, with and without correlation. Results are in eV and we employ the notation of Ref. 41.

	Hartree–Fock			With correlation		
Level	1st	2nd	3rd	1st	2nd	3rd
Γ_1	−52.7	2.21		···	0.36	
Γ_{15}	−22.9	32.9		−21.8	31.1	
X_1	−52.6	15.5		···	13.8	
X'_4	−23.2	10.4		−22.1	8.6	
X'_5	−22.9	19.8		−21.8	18.0	
L_1	−52.5	9.99		···	8.14	
L'_2	−23.3	8.10		−22.2	6.25	
L'_3	−22.9	28.5		−21.8	26.7	
K_1	−52.5	−23.1	11.8	···	−22.0	10.0
K_3	−23.1	11.4		−22.0	0.6	
K_4	−22.9	21.7		−21.8	19.9	

TABLE V. Energies of points of high symmetry for the krypton band structure, with and without correlation. Results are in eV and we employ the notation of Ref. 41.

	Hartree–Fock			With correlation		
Level	1st	2nd	3rd	1st	2nd	3rd
Γ_1	−31.9	2.66		···	1.27	
Γ_{15}	−13.8	31.3		−12.3	29.9	
Γ'_{25}	10.6	38.3		9.2	36.9	
Γ_{12}	13.2	44.2		11.8	42.8	
X_1	−31.3	5.07	21.5	···	3.68	20.1
X'_4	−15.2	10.6		−13.5	9.2	
X'_5	−14.1	17.1		−12.5	15.7	
X_3	6.85	34.0		5.46	32.6	
X_2	15.1			13.7		
X_5	15.7			14.3		
L_1	−31.4	5.92	18.4	···	4.53	17.0
L'_2	−15.4	8.61		−13.7	7.22	
L'_3	−13.8	37.4		−12.3	36.0	
L_3	10.1	15.1	37.2	8.7	13.7	35.8
K_1	−31.4	−14.5	6.21	···	−12.9	4.82
K_2	14.8			13.4		
K_3	−14.9	10.0	17.1	−13.3	8.6	15.7
K_4	−14.0	12.7	21.3	−12.4	11.3	19.9

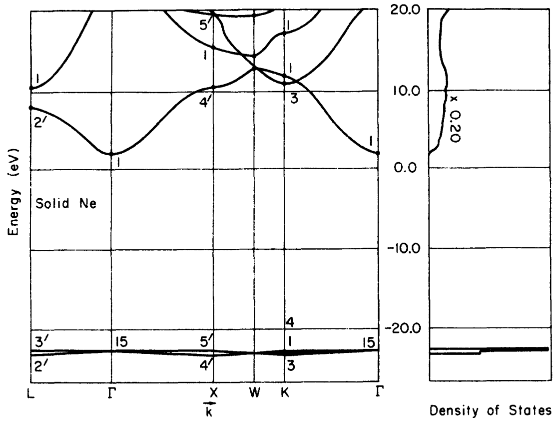

FIG. 1. Hartree–Fock band structure for solid Ne. Results are in eV and we use the BSW notation (Ref. 41). The density of states is also shown.

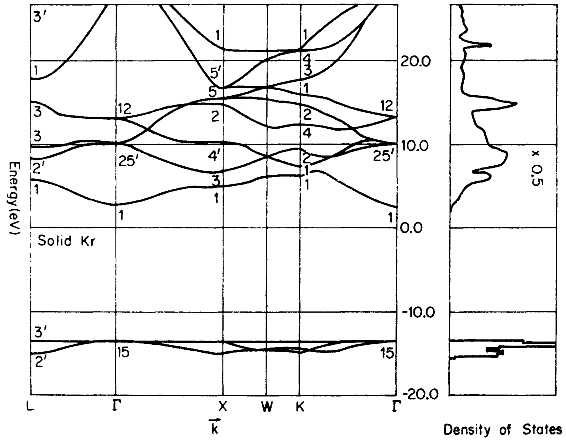

FIG. 3. Hartree–Fock band structure for solid Kr. Results are in eV and we use the BSW notation (Ref. 41). The density of states is also shown.

computes classically the energy involved in polarizing the surrounding atoms in a self-consistent way. Fowler predicts that such effects will reduce the Hartree–Fock band gap by about 2 eV for a rare-gas solid. This theory is appealing because of its simplicity and the economical nature of the required calculation. On the other hand, it has the defect of being a static limit and neglects the spatial extent of the electronic wave functions. The corrections in this theory are of course $\vec{k}$ independent. Lipari and Fowler have shown[6] that there are important $\vec{k}$-dependent corrections in the correlation effects for the solid-Ar valence band.

The model employed by Lipari and Fowler[6] in their calculation for solid Ar avoids the deficiencies of the simpler Fowler model.[16] In the model employed by Lipari and Fowler one replaces the exchange part of the Fock operator with a nonlocal screened exchange operator and a Coulomb-hole self-energy operator. This is done in accordance with the method developed by Hedin[39] and later used on silicon by Brinkman and Goodman.[40] This model also predicts that correlation-polarization effects reduce the optical band gap of solid Ar by a few eV. This model predicts that the conduction-band correlation corrections are $\vec{k}$ independent, but it finds that there are $\vec{k}$-dependent correlation-polarization corrections for the valence-band structure. In general one observes a tendency to substantially narrow the valence bands when correlation effects are included. The $\vec{k}$ independence of the correlation-polarization corrections for the conduction levels is not understood easily in this model. From the standpoint of one interested in calculations of this type the chief difficulty of this model is that it is quite inefficient in terms of computer time. This is because it is necessary to

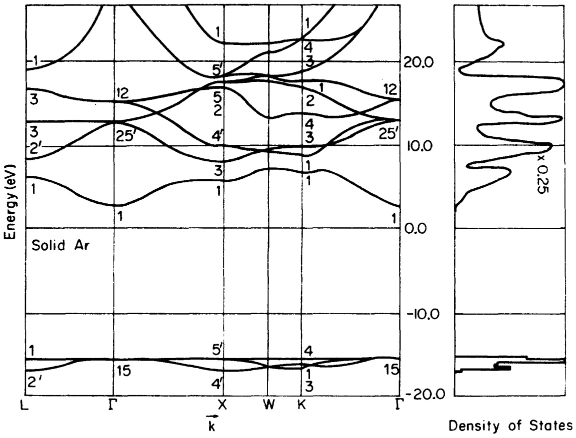

FIG. 2. Hartree–Fock band structure for solid Ar. Results are in eV and we use the BSW notation (Ref. 41). The density of states is also shown.

TABLE VI. Calculated values (present work) for the effective masses of electrons at the bottom of the conduction band and holes at the top of the valence band. Masses are in units of electron masses. Experimental numbers are from Refs. 3 and 25. (CB is the conduction band; VB is the valence band.)

Substance	Level	Direction	Effective mass	Expt.
Ne	Γ_1 CB	isotropic	0.802 ± 0.001	0.52
Ne	Γ_{15} VB	Δ_5	24.8 ± 0.1	
Ne	Γ_{15} VB	Δ_1	6.16 ± 0.01	
Ar	Γ_1 CB	isotropic	0.488 ± 0.001	0.47
Ar	Γ_{15} VB	Δ_5	11.6 ± 0.1	
Ar	Γ_{15} VB	Δ_1	1.93 ± 0.01	
Kr	Γ_1 CB	isotropic	0.418 ± 0.001	0.41
Kr	Γ_{15} VB	Δ_5	7.66 ± 0.01	
Kr	Γ_{15} VB	Δ_1	1.21 ± 0.01	

compute the band structure two times. The first time is to obtain the Hartree–Fock band structure which is used to provide needed parameters for the calculation of the Coulomb-hole operator and the screened exchange operator. One then must recompute the band structure using the correlated operator.

In the present calculation, we compute our correlation-polarization corrections by means of the electronic polaron model.[14,15] This model combines the quantitative features one gets from the Hedin model[39] with the speed of the simple Fowler model[16] to a desirable extent. In this model one finds for example that the conduction electron has an effective Hamiltonian given by[14]

$$\mathcal{H} = \sum_{\vec{k}} \epsilon_{\vec{k}} C_{\vec{k}}^\dagger C_{\vec{k}} + \hbar\omega_{ex} \sum_{\vec{K}} b_{\vec{K}}^\dagger b_{\vec{K}} - e[(2\pi\hbar\omega_{ex}/V)(1-1/\epsilon_\infty)]^{1/2} \times \sum_{\vec{K}} \frac{i}{|\vec{K}|}(b_{\vec{K}} e^{i\vec{k}\cdot\vec{r}} - b_{\vec{K}}^\dagger e^{-i\vec{k}\cdot\vec{r}}) . \quad (14)$$

In Eq. (14), V is the crystal volume, C and $C^\dagger$ are the electron annihilation and creation operators, b and $b^\dagger$ are the annihilation and creation operators for a longitudinal exciton and $\hbar\omega_{ex}$ is the energy needed to create such an exciton, and $\epsilon_{\vec{k}}$ is the Hartree–Fock energy of the band in question. One has a similar effective Hamiltonian describing the correlation of holes. In this model the energy of a conduction electron, $E_{n\vec{k}}$, is found to be

$$E_{n\vec{k}} = \epsilon_{n\vec{k}} + \sum_{\vec{K},m} \frac{|V_{\vec{K}}^{nm}|^2}{\epsilon_{n\vec{k}} - \hbar\omega_{ex} - \epsilon_{m(\vec{k}-\vec{K})}} , \quad (15)$$

and the energy of a valence hole, $E_{n\vec{k}}$, is seen to be

$$E_{n\vec{k}} = \epsilon_{n\vec{k}} + \sum_{\vec{K},m} \frac{|V_{\vec{K}}^{nm}|^2}{\hbar\omega_{ex} + \epsilon_{n\vec{k}} - \epsilon_{m(\vec{k}-\vec{K})}} \quad (16)$$

and

$$V_{\vec{K}}^{nm} = e\left(\frac{2\pi\hbar\omega_{ex}(1-1/\epsilon_\infty)}{V}\right)^{1/2} \times \frac{i}{|\vec{K}|}\int \phi_n^*(\vec{r})\,\phi_m(\vec{r})\,e^{i\vec{K}\cdot\vec{r}}\,d\vec{r} . \quad (17)$$

In the expression, Eq. (15), for the conduction electron, the $\vec{K}$ summation is over the first Brillouin zone and the m summation is over the conduction levels. In practice, one need only sum over the conduction levels close in energy to the one in question. In the expression, Eq. (16), for the valence hole the $\vec{K}$ summation is over the first Brillouin zone and the m summation is over the valence bands. The ϕ_n are either local orbitals or Wannier functions for the nth band.

Qualitatively, one sees from Eqs. (15) and (16) that owing to the correlation-polarization corrections, insofar as the bandwidths are less than $\hbar\omega_{ex}$, as is usually the case, the conduction band is lowered and the valence band is raised. This is in good agreement with the results of Fowler[16] or Lipari and Fowler.[6] One also sees from Eq. (16) that the top of the valence band will be raised by less than the bottom of the valence band, thus narrowing the valence band as Lipari and Fowler[6] find. This argument is based upon consideration of the energy denominator in Eq. (16) and upon the finite number of valence levels to be included in the summation. A similar argument cannot be advanced for the conduction levels since no matter how high one rises in the conduction band there is an infinite number of levels to sum over at each point in $\vec{k}$ space which lie higher than the level being computed, whereas there is only a finite number of levels lying lower to be summed over per point in $\vec{k}$ space. Thus there exists little or no reason to expect the correlation corrections for the conduction levels to be $\vec{k}$ dependent. This is in accordance with the findings of Lipari and Fowler[6] and may explain the previously noted absence of dispersion in the correlation corrections for the Ar conduction band.

We present a table of energies of selected points of high symmetry in the solid-Ne band structure in Table III, for solid Ar in Table IV, and for solid Kr in Table V. We note that for solid Ar the magnitude of the corrections we compute agree reasonably with those found by Lipari. In Fig. 4 we show the correlated band structures for solid Ne, Ar, and Kr.

III. COMPARISON WITH OTHER CALCULATIONS

In this section we shall attempt to make a detailed comparison of our Hartree–Fock results with those of other calculations. In order to assess the validity of our approach and also to attempt to understand the consequences of the other Hartree–Fock-type calculations, we shall place the greatest emphasis on the various available Hartree–Fock-type calculations. We shall also compare results with the calculations by Rössler[3] which employ a statistical-exchange approximation to the exchange potential and which are reasonably typical of the results obtained with this type of calculation.

A. Neon

There exist only three calculations for solid Ne of which the authors are aware. These are the present calculations, the Hartree–Fock calculations of Dagens and Perrot,[5] and the statistical-exchange calculations of Rössler.[3] We show the results of these three calculations in Fig. 5 for the line between Γ and X in the Brillouin zone. We employ here the BSW notation.[41] In our Ne calculation, we employed only an s, p basis set so that

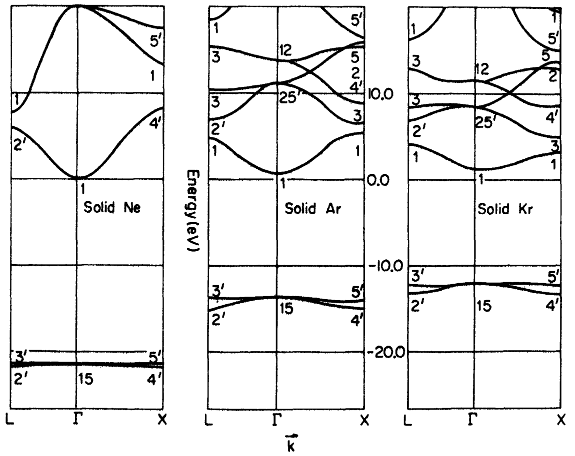

FIG. 4. Energy band structure of solid Ne, solid Ar, and solid Kr. These band structures include polarization-correlation corrections. Results are in eV and the BSW notation (Ref. 41) is employed.

there are obvious differences between our results and those of Dagens and Perrot, which include *d* and *f* levels as well. Nonetheless, we find quite good agreement between our calculation and that of Dagens and Perrot for those levels primarily associated with *s* or *p* levels in both the valence and conduction band.

A quantitative measure of this goodness is seen from a comparison of a few representative quantities. We find the top of the valence band, Γ_{15}, to lie at -1.69 Ry while Dagens and Perrot find it to lie at -1.67 Ry. We find the bottom of the conduction band to be Γ_1 and to lie at 0.17 Ry, while Dagens and Perrot find it to lie at 0.20 Ry. Thus the band gap in our calculation is 1.86 Ry (25.2 eV), and 1.87 Ry in the calculation of Dagens and Perrot. We find the extremal width of the valence band to be 0.03 Ry and Dagens and Perrot find it to be 0.036 Ry.

This level of agreement is no longer found when one considers the results of Rössler. This is partially due to the fact that Rössler has employed the constant part of the muffin-tin potential as an adjustable parameter with which to match experiment. In this case Rössler forces the band gap of Ne to be 20.75 eV. There are other differences apparent from Fig. 5. These are that the conduction-band structure is compressed in the statistical-exchange approximation compared to the Hartree–Fock band structures.[3,42]

B. Argon

Solid argon has received the most extensive attention of the solid rare gases. Hartree–Fock calculations have been reported by Lipari and Fowler,[6] Dagens and Perrot,[5] Lipari,[7] and Mickish and Kunz.[9] The latter two are self-consistent, but do not include in any detailed way many-body corrections. There have been reported calculations for solid Ar employing a statistical-exchange approximation by Knox and Bassani,[1] Mattheis,[2] Rössler,[3] and Lipari and Fowler.[6] By way of comparison we show in Fig. 6 the band structures for solid Ar along the line Γ-X from the present calculation, the calculation of Lipari, the calculation of Dagens and Perrot, and the calculation of Rössler. It is quite clear from Fig. 6 that there are substantial differences between the Hartree–Fock type of calculation and that of Rössler. Since Rössler uses the constant part of the muffin-tin potential as a parameter to match the optical band gap, the differences among the calculations in this respect are expected. However the extensive compression of the conduction-band structure in Rössler's calculation is significant. We note that the use of a muffin-tin-type potential alone cannot be the cause of such a difference since the other calculations employing a statistical-exchange approximation find such a compression to a great extent also. We note that in the present calculation, we employ a basis of *s*, *p*, and *d* orbitals and the over-all agreement of our band structure with that of Lipari or Dagens and Perrot is good. In fact it is much better than for Ne, where we employed a more limited basis. The principal differences come high in the conduction structure and are due to the presence of the predominantly *f*-like Γ_2' and Γ_{15} states included in the Lipari or Dagens and Perrot calculation.

A few representative numbers are interesting.

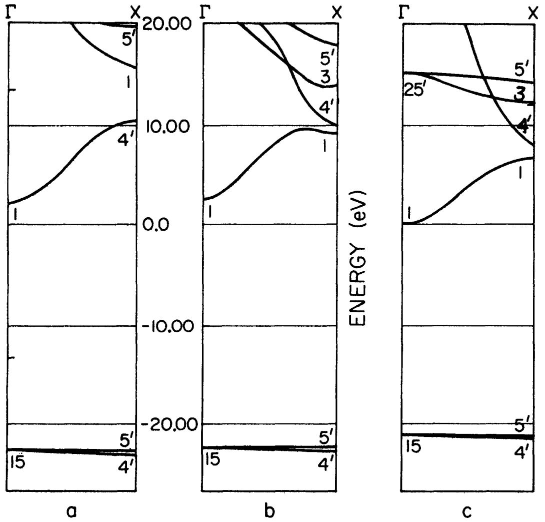

FIG. 5. A set of comparative band structures for solid Ne. In part (a) we show our Ne, Hartree–Fock result. In part (b) the results of Dagens and Perrot (Ref. 5) are shown and in part (c) the results of Rössler (Ref. 3) including recent corrections (Ref. 42). The BSW notation is used (Ref. 41).

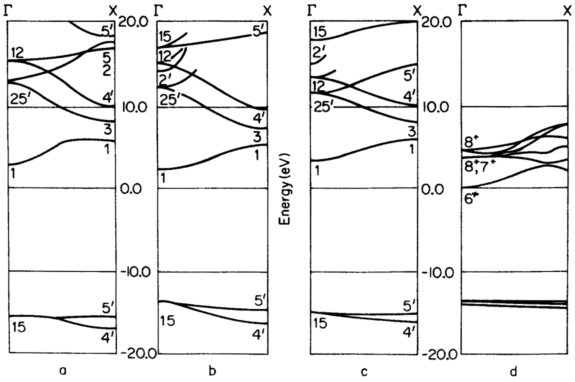

FIG. 6. A set of comparative band structures for solid Ar. In part (a) our Hartree–Fock bands are seen, in part (b) the results of Lipari (Ref. 7) are seen, in part (c) the results of Dagens and Perrot (Ref. 5) are seen, and in part (d) the results of Rössler (Ref. 3) are seen.

In the present calculation the Γ_{15} valence level is at -1.154 Ry and the Γ_1 conduction level is at 0.206 Ry, the band gap is 1.360 Ry (18.5 eV), the splitting of the Γ_1 from the Γ_{25}' conduction level is 0.749 Ry, the splitting of the Γ_{12} from the Γ_{25}' conduction level is 0.201 Ry, and the valence bandwidth is 0.096 Ry. In the calculation of Dagens and Perrot the same numbers are -1.116, 0.245, 1.361 (18.5 eV), 0.611, 0.222, and 0.089 Ry, respectively. According to Lipari these quantities are -1.025, 0.176, 1.201(16.4 eV), 0.724, 0.208, and 0.195 Ry, respectively. In the earlier work of Lipari and Fowler, these quantities are given as -1.025, 0.165, 1.190 (16.20 eV), 0.756, 0.187, and 0.197 Ry. We do not have available all these quantities from the calculation of Rössler; however, a few of them are available. Rössler forces a band gap of 1.015 Ry (13.80 eV), resulting in a separation of the Γ_1 and Γ_{25}' conduction level of 0.312 Ry and a separation of the Γ_{25}' and Γ_{12} conduction level of 0.125 Ry. These figures are sufficient to illustrate the severe compression of the solid-Ar conduction band in the statistical-exchange approximation as compared to the Hartree–Fock-type calculations. We discuss the reasons for the variations in the Hartree–Fock results after the discussion of krypton.

C. Krypton

Krypton has also received considerable attention from the band theorists. In addition to the present calculation, Lipari has also reported a Hartree–Fock calculation for solid Kr.[8] This calculation of Lipari is not self-consistent. In addition, Fowler[4] and Rössler[3] have reported calculations for solid Kr. The calculations of Fowler and Rössler are not self-consistent and employ the statistical-exchange approximation. By way of comparison, we show the band structures of Lipari and of Rössler as well as our present results in the direction Γ-X in Fig. 7.

It is interesting to compare a few representative numbers for these calculations. For each stated quantity we give the result found in our present calculation, the result found by Lipari, the result found by Rössler, and the result found by Fowler, respectively. The top of the valence band, Γ_{15}, is found to lie at -1.011, -0.949, -0.838, and -1.144 Ry. The conduction-band minimum, Γ_1, is found to lie at 0.196, 0.163, 0.000, and -0.302 Ry. The band gaps are therefore 1.207 (16.4 eV), 1.112 (15.2 eV), 0.838 (11.4 eV), and 0.842 Ry (11.4 eV). We see that the principal effect of the use of an adjustable parameter in Rössler's calculation is to decrease the optical band gap slightly with respect to the Fowler calculation which employs no adjustable constants. The width of the valence band, Kr $4p$ level, is found to be 0.122, 0.208, 0.09 including spin-orbit splitting, and 0.091 Ry. The splitting of the Γ_1 conduction minimum from the lowest Γ_{25}' d state is found to be 0.583, 0.616, 0.360, and 0.534 Ry. Finally the splittings of the lowest Γ_{25}' conduction level from the Γ_{12} conduction level is found to be 0.191, 0.147, 0.096, and 0.133 Ry.

As in the case of solid Ar, we find that the conduction levels in solid Kr are compressed in the statistical-exchange-approximation calculations when compared to the Hartree–Fock calculations. This effect is most noticeable in the calculation of Rössler. One curious effect is noticed. That is, when one compares the calculations of Rössler for

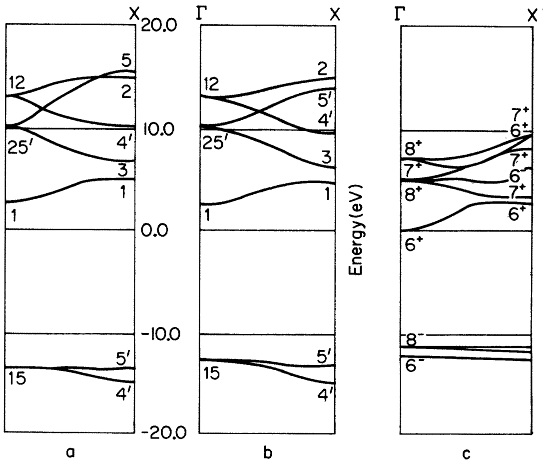

FIG. 7. A set of comparative band structures for solid Kr. In part (a) our Hartree–Fock bands are seen, in part (b) the results of Lipari (Ref. 8) are found, and in part (c) the results of Rössler (Ref. 3) are seen.

solid Ar and Kr one sees that the conduction levels are more compressed for Ar than for Kr. However in the Hartree–Fock calculations of the present authors and of Lipari one finds the reverse effect is true. That is, one finds the Ar conduction bands more widely spread than for those of Kr. In Sec. III D we will argue that this deviation in trends is significant and that experiment favors the Hartree–Fock calculations, rather than the calculations of Rössler which employ a statistical-exchange approximation.

D. General Considerations

In this section we attempt to come to terms with the differences among the several calculations considered. We consider first the differences among the various Hartree–Fock types of calculations. Basically, the following conclusions can be made. The valence bands obtained in the present calculation agree well in width, form, and position with those found by Dagens and Perrot.[5] The valence bands computed by Lipari[7,8] and Lipari and Fowler[6] are found to lie higher and be broader than those in the present calculation. Rössler[3] has advanced a series of arguments which tends to prove that the valence bands computed by Lipari and Fowler lie as high as they do and are as wide as they are because of the poor convergence of the plane-wave expansions which are employed by Lipari and Fowler. We find the arguments advanced by Rössler to be reasonable and believe the valence bands obtained in this calculation or that of Dagens and Perrot accurately represent the Hartree–Fock valence-band structure of the rare-gas solids.

We find the case of the conduction bands to be rather different. Here we find good agreement among the available Hartree–Fock calculations with respect to the predominantly *s*- or *p*-type conduction levels. We find that the agreement is poorer with respect to the *d*-type levels. With respect to the *d*-type levels, one sees that the present results agree well with the results of Lipari and agree less well with those of Dagens and Perrot. In general the *d* levels of Dagens and Perrot lie lower than do those of Lipari or our present results. We argue that this may be due to the muffin-tin-type potential employed by Dagens and Perrot. We argue as follows: The potential about a single nuclear site in a solid rare gas when expanded in spherical harmonics has nonzero coefficients for the Y_0^0 term and the Y_4^m terms as well as for higher-series members. In the muffin-tin type of potential in the region about a given nucleus (i.e., in the muffin) one allows only a Y_0^0 term. Now *s* or *p* functions see only a Y_0^0 term in any case due to the orthogonality and multiplication properties of spherical harmonics, but the *d*-type functions also directly see the Y_4^m-type terms. Therefore we anticipate that the *d* bands would be much more sensitive to a muffin-tin potential than would the *s* or *p* bands. We note that a similar observation can be made in the case of the krypton calculations employing a statistical-exchange approximation. In this case, the non-muffin-tin calculation of Fowler finds a much greater *s*-*d* band separation than does Rössler, who employs a muffin-tin calculation.

In previous work on the alkali halides, it has been suggested that this discrepancy between muffin-tin and non-muffin-tin calculations with respect to the *d* bands may be due to the poor convergence of the plane-wave expansions used for the non-muffin-tin calculation as opposed to the KKR- or APW-type calculations used with the muffin-tin calculations.[43] We argue that this is unlikely to be the source of difficulty. We find good agreement here between our results which do not employ a plane-wave expansion and are not limited by the arguments advanced by Overhof for plane-wave expansions and the results of Lipari and Fowler[6] and Lipari.[7,8] This good agreement is quite apparent in the case of solid Ar, where both calculations are self-consistent, and is essentially as good for Kr and the earlier non-self-consistent Ar calculation of Lipari and Fowler. In previous work, Kunz, Fowler, and Schneider[44] investigated this point for NaCl. They compared OPW results obtained using both muffin-tin and non-muffin-tin potentials and found good agreement in both the *s* and *d* bands with the muffin-tin APW calculation of Clark and Kliewer[45] when Kunz *et al.* used a muffin-tin potential, and similar discrepancies as found in this calculation when they did not use a muffin-tin-type potential. Thus we do not believe that convergence problems are responsible for the disagreement of the muffin-tin- and non-muffin-tin-type results for the conduction *d* bands.

An issue which would be interesting to understand is the great disagreement between the Hartree–Fock energy bands and the bands obtained using a statistical-exchange approximation. It may be argued that the statistical-exchange approximation actually includes some correlation effects and hence should not be expected to agree with Hartree–Fock results.[46] This is not an unreasonable argument. However, it is clear that when one incorporates correlation effects into Hartree–Fock energy bands as has been done in the present calculation or in the calculation of Lipari and Fowler,[6] one would expect better agreement than with bands obtained in a statistical-exchange approximation. Excepting the band gap, which is sometimes parametrized in statistical-exchange calculations, the agreement does not improve at all. We are unable to quantitatively explain this continued disagreement.

IV. COMPARISON WITH EXPERIMENT

The comparison of band-structure calculations with experiment for the solid rare gases is difficult. This is because very little is known about the band structures of such solids from an experimental viewpoint other than the size of the energy band gap. It is true, however, that there are detailed optical spectra available for the solid rare gases. However, the low-lying optical properties of these solids are dominated by excitonic effects. In addition, the low-lying band-to-band transitions have their strengths greatly modified by exciton effects.[47] In addition to such effects, Lafon and Fouquet[48] have recently shown that the transition matrix elements at or near the band-to-band threshold are strongly enhanced by symmetry effects. Thus we expect to find little resemblance between the joint density of states for valence-to-conduction transitions and the measured optical spectrum. In the soft-x-ray region the situation is rather different. Here Rössler[3] has found that the energy-band structure provides a reasonable basis for interpreting the observed spectrum. He finds that exciton effects are secondary in importance in this spectral region for the solid rare gases. There exists, in addition, alloy data for NeAr and ArKr crystals in the soft-x-ray region. We find this data may be decisive in choosing from among the available band models. Finally, the effective masses of the conduction-band electrons are known. We now consider separately the experimental situation for Ne, Ar, and Kr, and then the alloy data.

A. Solid Neon

Recently solid Ne has been studied in the vacuum-ultraviolet or soft-x-ray region in the valence-to-conduction-band transition region by Haensel *et al.*,[22] and in the vicinity of the L_{I} edge by Keitel.[23,25] In the measurements of Haensel *et al.* Ne was found to have strong exciton absorption at about 17.8 eV continuing to an inferred series limit for the excitonic transition of just under 22 eV. Therefore we may reasonably say the optical band gap of solid Ne is about 22 eV. In the present calculation using Hartree–Fock theory, the band gap is found to be 25.2 eV. If we use the band gap we compute, including the polarization-correlation corrections, the predicted band gap becomes 22.3 eV. This agreement is quite acceptable.

We also can gain a theoretical estimate of the exciton binding energy by use of effective-mass theory. It is not really expected that such a method is very accurate for the $n=1$ exciton in a substance as tightly bound as Ne; nonetheless, it may provide reasonable results for the higher members of the exciton series. In this theory the exciton binding energy (i.e., the amount of energy the exciton lies below the conduction minimum) is found to be

$$E_B = -\frac{me^4}{2K^2}\frac{1}{\hbar^2 n^2} \cdot \qquad (18)$$

K is the optical dielectric constant, m the effective mass for the exciton, n the principal quantum number. Thus we predict the binding energy of the $n=1$ exciton to be 6.7 eV, for the $n=2$ exciton, 1.7 eV, and for the $n=3$ exciton, 0.7 eV. In the measurements of Haensel *et al.* the binding energies are found to be about 3.7 eV for the $n=1$ exciton, 1.2 eV for the $n=2$ exciton, and 0.6 eV for the $n=3$ exciton from reflectivity data. Part of the discrepancy may be due to our value of the effective mass for Γ_1, which is poorer for Ne than for Ar or Kr. This may be due to the limited basis set which we employ for solid Ne.

We have computed the joint density of states for transitions from the valence band and the L_{I} shell. These are shown in Figs. 8 and 9 along with the pertinent experimental data. In this regard there is little to be said since in both cases the theoretical predictions are for flat featureless absorption spectra. This flat featureless structure is just what is found here except for the presence of exciton lines. It is interesting, however, to note the antiresonance quality of the exciton absorption in the L_{I} edge. This interesting feature is well understood as an interference phenomena between the L_{I}-shell exciton structure and transitions from the valence levels to states high in the conduction band which are energetically about degenerate with the L_{I}-shell exciton absorption.[23]

B. Solid Argon

Solid Ar has been studied in the vacuum-ultraviolet region by Baldini,[20] by Haensel *et al.*,[21,24] and by Keitel.[25] Studies in the soft-x-ray region

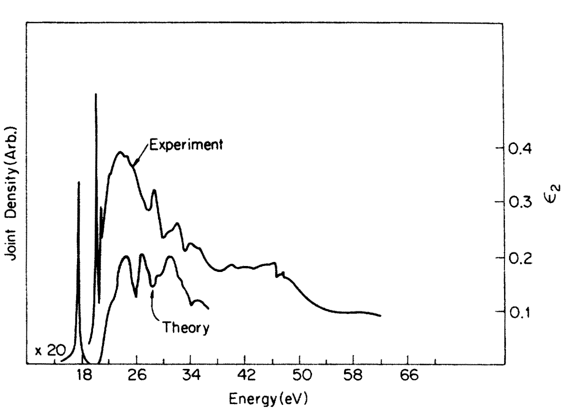

FIG. 8. Theoretical joint density of states for transitions from the Ne valence band from our calculation. An experimental determination of the reflectivity is also shown (Ref. 22).

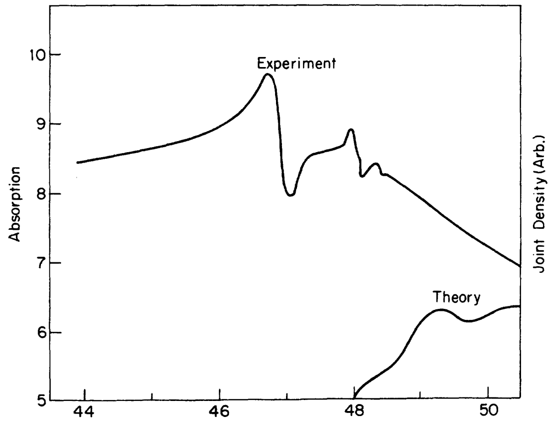

FIG. 9. Theoretical joint density of states for transitions from the Ne L_I shell from our calculations. An experimental determination of the spectrum is also shown (Ref. 25).

have been performed by Haensel *et al.*[24] and by Keitel.[25] In the vacuum-ultraviolet region solid Ar is seen to have fundamental excitonic absorption at about 12.10, 12.35, and 12.50 eV, and a Rydberg series of exciton transitions with members at 13.58, 13.75, 13.90, 14.03, and 14.09 eV.[21] Apparently the Rydberg series converges to a band-to-band transition at about 14.2 eV. Thus the experimental band gap is 14.2 eV. In our Hartree–Fock calculation we find the band gap of solid Ar to be 18.5 eV. When we use our correlated values for the band structure, the predicted band gap is seen to reduce to 15.2 eV, a figure in reasonable agreement with experiment. Another available quantity is the experimental value of the effective mass of an electron at the Γ_1 conduction minimum. From our calculation we are able to compute this quantity to be 0.488 ± 0.001 electron masses, (see Table VI). By careful analysis of optical data and assuming a heavy mass for the valence hole, Rössler finds the experimental value of the conduction effective mass to be 0.47 electron masses.

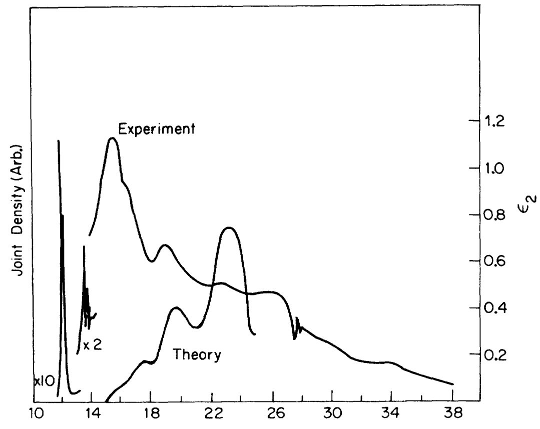

FIG. 10. Theoretical joint density of states for transitions from the Ar valence band from our calculations. An experimental determination of the spectrum is also shown (Refs. 21, 24, and 25).

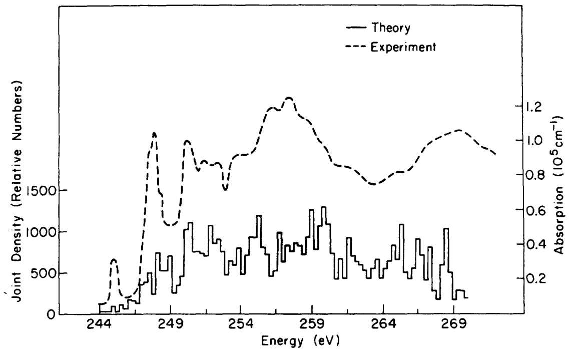

FIG. 11. Theoretical determination of the joint density of states for transitions from the Ar $L_{II,III}$ level from our calculation. An experimental spectrum is shown (Ref. 24).

Just as in the case of solid Ne, we are able to deduce the binding energy of the excitons approximately by using effective-mass theory. We find the binding energy of the $n = 1$ exciton to be 2.6 eV, of the $n = 2$ exciton to be 0.65 eV, of the $n = 3$ exciton to be 0.29 eV, and of the $n = 4$ exciton to be 0.16 eV. Experimentally, these quantities are 2.30, 0.58, 0.26, and 0.07 eV.[21]

We have computed the joint density of states for transitions from the valence band and from the $L_{II,III}$ shell. These are shown in Figs. 10 and 11 along with the pertinent experimental data. In the case of transitions from the valence band, we observe poor agreement with respect to relative peak heights between theory and experiment. This point is discussed at the beginning of this section and is as expected. What is also seen from Fig. 10 is that there exists a reasonable one-to-one correspondence between peak positions in the theory and the experiment. This is as it should be if all is well. We note that in preparing this figure, the theoretical data has been positioned energetically by calculation and no shifting of energies has been done to enhance the agreement. In the case of the $L_{II,III}$ spectrum, we compute the joint density of states using the experimental value of the spin-orbit splitting of the argon $2p$ shell.[24,25] We weighed the initial states 2 : 1 to account for the degeneracy of the core state. In this case we have not computed the absolute onset of absorption due to the neglect of strong outer-shell relaxation effects for the central-cell atom in our calculation. We have therefore adjusted our calculated joint density energetically to match the experimental

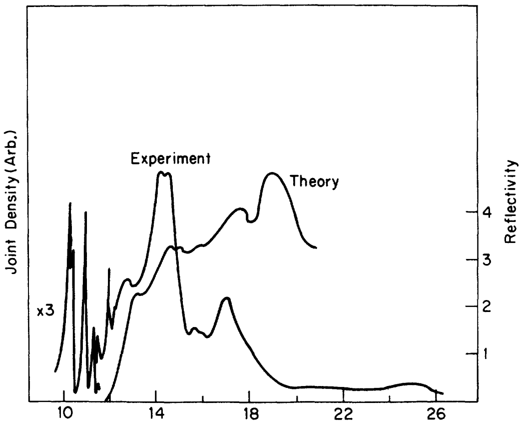

FIG. 12. Theoretical joint density of states for transitions from the Kr valence band from our calculation. An experimental spectrum is also shown (Ref. 49).

broad absorption feature between 255 and 259 eV to a similar one in our calculation. The over-all agreement is acceptable. We find here, as has Rössler,[17,18] that one basically is able to interpret the $L_{\text{II,III}}$ spectrum from the state density, except for exciton or electron-hole edge enhancement effects near the onset of absorption.

C. Solid Krypton

Solid Kr has been studied in the vacuum-ultraviolet region by Baldini[20] and by Haensel *et al.*[49] Studies in the soft-x-ray region have been performed by Haensel *et al.*[27] and Schreiber.[26] In the vacuum-ultraviolet region, solid Kr is seen to have fundamental excitonic absorption at about 10.25 eV with a spin-orbit partner 0.6 eV higher and two Rydberg series, one for each of the spin-orbit-split valence bands. From the data of Haensel *et al.* we infer that the optical band gap is about 12 eV.[49] The value we compute for the band gap using Hartree–Fock theory is 16.4 eV. The value we compute, using our correlation-polarization corrections, is 13.4 eV. In the case of solid Kr, atomic number of 36, the valence band is spin-orbit split at the Γ point by 0.6 eV. If one includes spin-orbit effects the predicted band gap is reduced to 13.2 eV. Furthermore, the valence band is p like while the conduction band is s like and we anticipate a further reduction in the predicted band gap if one were to include further relativistic effects. This situation is similar to some alakli halides we have studied previously.[30] Another quantity which is experimentally available is the effective mass of conduction electrons at the bottom of the conduction band. This is given as 0.41 electron mass.[3] We have computed this quantity (Table VI) and find it to be 0.418 electron masses.

We have computed the joint density of states for transitions from the valence band and from the $M_{\text{IV,V}}$ shell. These are shown in Figs. 12 and 13 along with the pertinent experimental data. In the case of the valence-band transitions, we observe poor agreement with respect to relative peak heights between theory and experiment. This is in accord with the discussion at the beginning of this section. We do, however, find a nearly one-to-one correspondence with respect to peaks and valleys between theory and experiment except at high energy, where the experience of Lafon and Fouquet has led us to expect our calculation to grossly overestimate the absorption.[48] In the case of the $M_{\text{IV,V}}$ spectrum, we compute the joint density of states using the experimental value of the spin-orbit splitting of the Kr $3d$ shell.[27,26] We weighed the initial states 3 : 2 to account for the degeneracy of the core state. In this case we do not compute the absolute onset of absorption owing to the neglect of important central-cell corrections for deep excitations in our model. We have adjusted our calculated structure energetically to match the broad dip in absorption between 96 and 100 eV with a similar feature in our calculation. The over-all agreement is acceptable. Again we find that one is able to interpret this spectrum basically from band theory except for strong exciton effects at threshold.

At this point a mystery arises which requires resolution. Rössler[3,17,18] has also computed the Kr $M_{\text{IV,V}}$ spectrum and finds a nearly equivalent degree of agreement. This is surprising in view of greatly different bands found for Kr. Rössler computes his spectrum using interpolation schemes, since his bands are only determined along symmetry lines. In addition, Rössler has interpolated the Kr bands of Lipari[8] and finds total disagreement between Lipari's spectrum and experiment. This is evident in the first 5 or 6 eV of the conduction state density. We find this sequence of calculations highly interesting since our computed band structures match those of Lipari[8] essentially exactly over the first 8 or 10 eV. Therefore we ex-

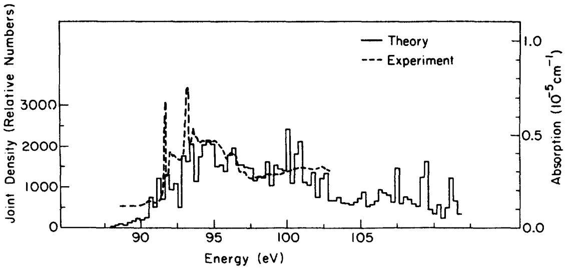

FIG. 13. Theoretical joint density of states for transitions from the Kr $M_{\text{IV,V}}$ level from our calculations. An experimental spectrum is also given (Refs. 26 and 27).

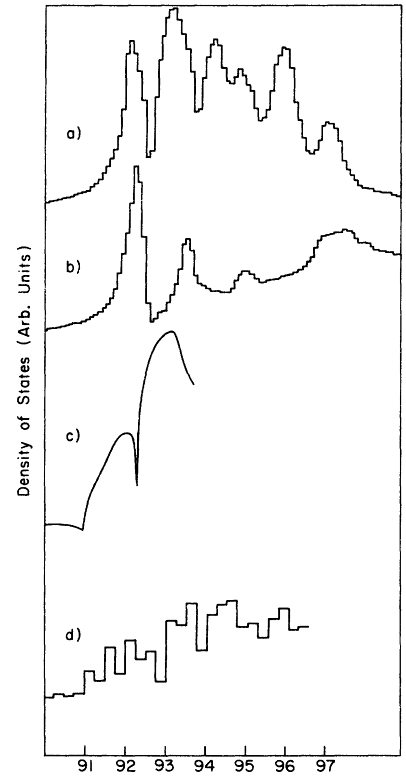

FIG. 14. A comparative set of theoretical determinations of the Kr $M_{\rm IV,V}$ joint density of states. In part (a) the joint density representing the bands of Rössler (Ref. 3) as interpolated by Rössler is seen (Refs. 17 and 18). In part (b) the joint density representing the bands of Lipari (Ref. 8) as interpolated by Rössler is seen (Ref. 18). In part (c) the joint density representing the bands of Lipari (Ref. 8) as interpolated by the present authors is seen. In part (d) the joint density calculated directly by the present authors and representing both the present calculation and that of Lipari (Ref. 8) is seen.

pect our band structure will yield the same state density as Lipari. This argument we believe is strengthened since we employ the same solid-state potential as Lipari. Of course in our present calculation we employ no interpolation and hence our results are far less subject to error than Rössler's. As a check, we have computed the state density for Lipari's Kr band structure using the same pseudopotential scheme we have been using for the alkali halides. The agreement between our interpolated results for the Lipari band structure and our computed results from our band structure is good. The total situation is summarized in Fig. 14. Here in part (a) we show the $M_{\rm IV,V}$ spectrum of Kr from Rössler's interpolation of Rössler's calculation. In part (b) we see the $M_{\rm IV,V}$ spectrum of Kr from Rössler's interpolation of Lipari's calculation. In part (c) we see the $M_{\rm IV,V}$ spectrum of Kr from our interpolation of Lipari's calculation. Finally in part

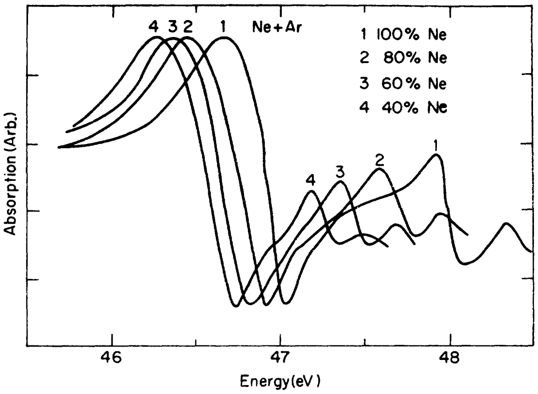

FIG. 15. Experimental spectra for alloys of solid Ne and solid Ar (Ref. 28).

(d) we find our direct calculation of the $M_{\rm IV,V}$ spectrum from our calculation, which should also be a good representation of Lipari's calculation. We find from this that Rössler has made a substantial error in interpolating the band structure of Lipari and has wrongly shown this calculation to be in error.[18] We are also unable to understand the agreement of our calculated $M_{\rm IV,V}$ spectrum of Kr (Fig. 14) and that of Rössler (Fig. 14) given the huge differences in the band structure (Fig. 7).

Perhaps one lesson to be learned from the different results from the interpolaton of Lipari's band structure by the authors and by Rössler is that constructing state densities by interpolating band structures computed at a few points or lines

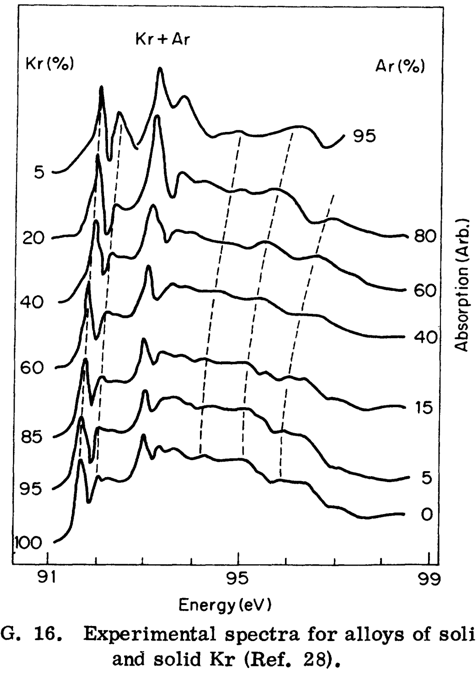

FIG. 16. Experimental spectra for alloys of solid Ar and solid Kr (Ref. 28).

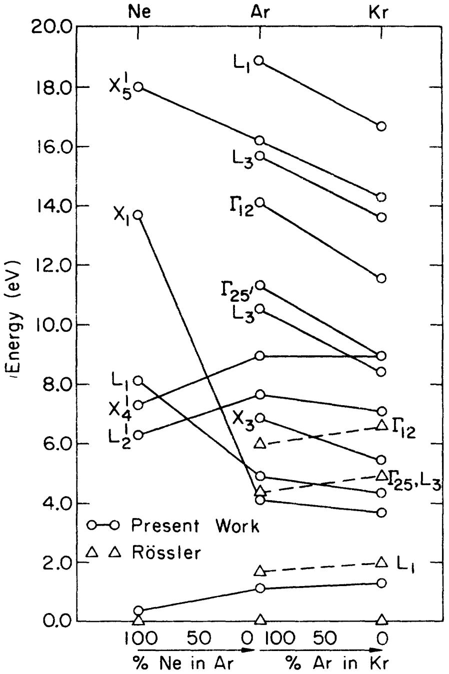

FIG. 17. How key levels in the conduction band shift as one goes from Ne to Ar to Kr. Results shown are for our present calculation, including many-body effects, and also from the calculation of Rössler (Ref. 3).

of high symmetry may be quite unreliable. In fact, one sees here for Kr that even granted a reasonable fit of the band-structure points computed by Lipari in the interpolations of the authors and of Rössler, the resulting state densities are not unique.

D. Alloy Data

Alloy studies for mixtures of Ne : Ar and Ar : Kr have been reported by Haensel *et al.*[28] In Fig. 15 we show their results for Ne : Ar mixtures in the Ne L_1-shell region. Owing to the featureless absorption except for the excitonic resonance-antiresonance lines we are unable to interpret this spectrum from band theory. In Fig. 16 we show the results for mixtures of Ar : Kr in the region of the Kr $M_{\mathrm{IV,V}}$ edge. We note the trend of given spectral features to move to higher energy as the mixture progresses from Kr to Ar. These trends as shown in the dashed lines in Fig. 16 are due to Haensel *et al.*[28] Previously we have noted that our computed conduction levels expand as we move from Kr to Ar. We also noted that the opposite effect is seen in the statistical-exchange-approximation calculations of Rössler.[3,28] We show these trends for key conduction levels in going from Ne to Ar to Kr from our calculation, including correlation-polarization corrections, in Fig. 17. We also show these trends from the calculation of Rössler. Thus we find our calculations are able to interpret the trends in the alloy data whereas those due to Rössler are not.

V. CONCLUSIONS

In this paper we have obtained *ab initio* band structures for Ne, Ar, and Kr. These calculations are obtained in the self-consistent restricted Hartree–Fock approximation. We also compute correlation corrections. We have found this method of calculation produces good results from an experimental viewpoint and employs no adjustable parameters. Not only have we succeeded in predicting band gaps but also in predicting to a high degree of accuracy such sensitive quantities as effective masses. Since the band model we developed is an efficient one, we are able to directly compute state densities and optical properties without needing the intermediary of pseudopotential interpolations or of tight-binding interpolations. This should allow much greater accuracy in assessing the experimental properties of a band structure, since an additional step separating the band structure from experimental prediction is removed.

We also conclude that such *ab initio* methods are a practical way of studying band structures in general. In this calculation we have handled an element of the third row in the Periodic Table (Kr) and we are able, using existing codes, to handle any element or compound of elements up through the fourth row of the Periodic Table. Also we are able to afford to compute large numbers of points in the Brillouin zone directly. In previous *ab initio* efforts by one of us (ABK) and others[5–8] this has been a major stumbling block in making such calculations practical since only a few band-structure points could be calculated directly. We are able to perform our total calculation using about one-half the computer time and far less computer memory than is needed for a much less extensive calculation using the methods of Lipari.[6–8] In fact we find our codes to be nearly as fast as some codes in current use to compute band structures using statistical-exchange approximations.

We find the Hartree–Fock band gaps to be greater than experiment, in accord with the predictions of Fowler.[16] We also find our Hartree–Fock valence bands to be wider than one obtains using a statistical-exchange approximation. Finally we find that correlation effects narrow the valence bands as was found by Lipari and Fowler.[6] To repeat, most important of all, we conclude that *ab initio* techniques represent a practical way of studying band structure.

ACKNOWLEDGMENTS

The authors wish to express their greatest appreciation to Professor B. Sonntag for a great number of useful discussions relating to the experimental situation in the solid rare gases. We also express our appreciation to the staff of the MRL Σ-5 computing center, and to James Smith in particular, for their assistance in this project. Finally we wish to thank Professor R. J. Maurer for his unstinting support of this research project.

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[*] Work supported in part by the National Science Foundation under Grant No. GH-33634, and by the Army Research Office under Contract No. DA-HC04-69-C0007, and by the Aerospace Research Laboratory, Air Force Systems Command, USAF, Wright-Patterson AFB, Ohio, under Contract No. F33615-72-C-1506.

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