PHYSICAL REVIEW B VOLUME 8, NUMBER 10 15 NOVEMBER 1973

One-Electron Theory of the Bulk Properties of Crystalline Ar, Kr, and Xe[†]

S. B. Trickey and F. R. Green, Jr.
Quantum Theory Project, Department of Physics and Astronomy, University of Florida, Gainesville, Florida 32611

Frank W. Averill
Department of Materials Science, Northwestern University, Evanston, Illinois 60201

(Received 8 June 1973)

The cohesive energy as a function of lattice constant and the P-V relation for Ar, Kr, and Xe have been calculated at $T = 0$ K in the static-lattice limit. The calculation employed the self-consistent augmented-plane-wave statistical-exchange (APW-$X\alpha$) method, which, except for our own preliminary work, has not heretofore been applied to the study of the bulk properties of a van der Waals crystal. The agreement with experiment is at least semiquantitative with respect to the cohesive energies. The comparison with extant PV data is acceptable. By use of a static-lattice sum of a pair-potential function with undetermined parameters, an effective pair potential is determined, with fairly realistic parameter values as a result. Comparison with other energy-band calculations shows that the occupied one-electron energies found in this calculation are in good agreement with those found by other workers. The conduction-band energies are not, a result that is usual in $X\alpha$ calculations. The over-all trends found in this calculation are related to those found by Averill in a recent APW-$X\alpha$ calculation on the alkali metals.

I. INTRODUCTION

Quantitative calculations of the binding energy of the rare-gas crystals (RGC), without resort to an intermolecular potential, were first attempted over 40 years ago.[1-4] Of necessity, these calculations employed a wide variety of simplifications and assumptions about the repulsive energies, the order of multipole terms retained, the values of atomic polarizabilities, etc. London's calculations[1] seemed to give reasonable agreement with experiment, but Deitz argued[3] (on the basis of the strong repulsion which he found) that this result was largely fortuitous. From 1935 until 1964 we are aware of no further work along these lines, though there developed (and continues to develop) an enormous literature on the calculation of the properties of the RGC from highly refined semiempirical interatomic potentials.[5-12] Then, in 1964, Linderberg and Bystrand[13] published the results of a calculation of the cohesive energy of fcc neon. Their treatment involved the tight-binding calculation[14] of the Hartree-Fock contribution to the cohesion and the calculation of the correlation corrections via approximate solution to the expressions obtained by Linderberg[15] from a study of the complex dielectric permeability. The lattice-dynamical contribution was obtained from empirical estimates and/or other calculations. Taken at face value, their computed cohesive energy was in good agreement with experiment. Unfortunately, certain simplifications (for example, the use of only a single d orbital) and restrictions rendered the calculated result unreliable.

For obvious reasons, the computational study of the energy bands of the RGC has been a much more active area of endeavor than has been the calculation of the cohesive properties. For argon there are many published calculations of the energy bands including those by Knox and Bassani[16] [non-self-consistent (non-SC), orthogonalized-plane-wave (OPW), local exchange], Mattheiss[17] [non-SC, augmented-plane-wave (APW), local exchange], Rössler[18] [non-SC, Korringa-Kohn-Rostoker (KKR), local exchange], Lipari and Fowler[19] (non-SC, OPW, Hartree-Fock, and local exchange), Ramirez and Falicov[20] (pseudopotential fit to Ref. 17), Kunz[21] (SC, local orbitals, Hartree-Fock), Dagens and Perrot[22] (non-SC, APW, Hartree-Fock), and Lipari[23,24] (SC, local orbitals, Hartree-Fock). There are substantially fewer papers concerning the energy bands of solid krypton: we are aware of four. In chronological order, they are by Fowler[25] (non-SC, OPW, local exchange), Lipari[26] (non-SC, OPW, Hartree-Fock), Rössler[18] (non-SC, KKR, local exchange), and Lipari[24] (SC, local orbitals, Hartree-Fock). Apparently there are only two published energy-band calculations on Xe, by Reilly[27] (non-SC, OPW, several local exchanges) and Rössler[18] (non SC, KKR, local exchange). We are also aware of a calculation by Boring[28] in which the band gaps resulting from three local-exchange approximations were compared in the context of a self-consistent APW treatment of Kr at the experimental lattice constant. [See also A. B. Kunz and D. J. Mickish, Phys. Rev. B 8, 779 (1973)].

In most cases, these calculations were in part evaluated (by their originators) by the classic tests of energy-band theory: the comparison of valence-band widths and the direct band gap to experimental optical properties. Such comparison usually resulted in the conclusion that the Hartree-Fock (HF) band gaps are too large, the statistical-exchange gaps too small. The situation is confused by the fact that several of the calculations are non-self-consistent, with the result that the calculated characteristics of the valence and conduction bands may be strongly influenced in these cases by the vagaries of the crystal potential. There is substantial disagreement, regarding both the *s*-*d* valence-band separation and the valence-band width in argon,[18,19,22] for example.

One major feature of the recent evolution of energy-band theory is the reemergence of interest in the use of the theory to calculate bulk properties for the crystalline ground state. Virtually all of this activity has been associated with the development of local exchange-correlation theories which postulate a total energy expression in terms of one-electron orbitals.[29] The first such self-consistent calculation appears to be due to DeCicco[30] who applied the APW method and the original Slater exchange approximation[29a,29b] to KCl. Since that time there have been several similar calculations on a variety of metallic solids, including the entire alkali series,[31] lithium,[32,33] aluminum,[34] iron,[35] and vanadium.[36] Though the agreement with experimental values of bulk properties found in these calculations was by no means perfect, it was sufficiently good in most cases to suggest that even the simplest local-exchange-correlation model (the $X\alpha$ model—see Sec. II) provides a nearly quantitative description of these metals and of the ionic insulator KCl. In consequence of these successes, the outcome of $X\alpha$ local exchange-correlation calculations of the RGC cohesive properties is of obvious interest, for if such calculations are successful, a new line of attack on the RGC binding problem has been found. On the other hand, if such calculations fail, a clear limitation has been found for the direct applicability of the model.

The question of the applicability of local exchange-correlation models to the problem of inert gas interactions has been raised by Konowalow *et al.*,[37] who used the so-called multiple-scattering $X\alpha$ method[29a,29b] to treat the neon diatom Ne_2. They reported finding a purely repulsive interaction, a result which, if correct, would make any further application of the $X\alpha$ model to rare-gas systems seem unwarranted. However, Connolly and Danese[38] motivated by our preliminary finding of binding in fcc Ar with the $X\alpha$ model,[39] have reexamined and extended the calculation of Ref. 37. They find that those results are unreliable because of failure to use double-precision arithmetic throughout the calculation. Further, their preliminary evaluation of certain "non-muffin-tin" corrections indicates that the repulsion of 0.0028 Ry/particle (at an internuclear separation of 6.0 bohr) obtained in the double-precision muffin-tin calculation is cancelled by non-muffin-tin corrections of − 0.0029 Ry/particle. Their results are limited, by the statistical error inherent in the numerical quadrature scheme they employ, to a precision of ± 0.0002 Ry/particle. Because of the weakness of the Ne–Ne attractive interaction, we regard it as the most difficult test (we exclude solid helium because of the dominance of quantum-crystal effects) for the $X\alpha$ model. In view of the preliminary nature of the work of Connolly and Danese, we defer reporting on fcc neon here and note only that we do find binding, just as reported below for Ar, Kr, and Xe.

In Sec. II we outline the structure of the $X\alpha$ model and discuss briefly both the choice of the parameter α and the numerical methods used. Our calculated energy vs. volume results for fcc Ar, Kr, and Xe are presented and the derived PV relations (at zero temperature) are treated in Sec. III. In Sec. IV we present the pair potentials obtained by fitting lattice sums to the calculated energy versus volume data. We give a brief discussion of the calculated energy bands in Sec. V and conclude with comments and summary in Sec. VI.

II. SUMMARY OF APW-$X\alpha$ MODEL: CALCULATIONAL PROCEDURES

For the total energy of a many-fermion system (we utilize a static lattice throughout our treatment) the $X\alpha$ model assumes[29] the expression

$$\langle E_{X\alpha}\rangle = \langle T_{X\alpha}\rangle + \langle W_{X\alpha}\rangle \; . \tag{2.1}$$

The quantities which appear in this expression are, in rydberg units,

$$\langle T_{X\alpha}\rangle = -\sum_i n_i \int u_i^*(1)\nabla_1^2 u_i(1)\,d\vec{r}_1 \; , \tag{2.2}$$

$$\langle W_{X\alpha}\rangle = \frac{1}{2}\sum_{\mu\nu}{}' g_{\mu\nu} + \sum_\nu \int \rho(1) g_{1\nu}\,d\vec{r}_1 + \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2\,\rho(1)\rho(2) g_{12} + \frac{1}{2}\int \rho(1) U_{X\alpha}(1)\,d\vec{r}_1 \; . \tag{2.3}$$

In turn, these quantities depend upon the one-electron spin orbitals u_i; their occupancies n_i; the Coulomb operators (Roman and Greek subscripts refer to electrons and nuclei, respectively)

$$g_{\mu\nu} = 2Z_\mu Z_\nu / r_{\mu\nu} \; , \tag{2.4}$$

$$g_{1\mu} = -2Z_\mu / r_{1\mu} \; , \tag{2.5}$$

$$g_{12} = 2/r_{12} \; ; \tag{2.6}$$

the charge density

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1) \; ; \tag{2.7}$$

and the local exchange-correlation operator, which for the non-spin-polarized case is

$$U_{X\alpha}(1) = -9\alpha(3/8\pi)^{1/3}\rho^{1/3}(1) \; . \tag{2.8}$$

The choice of the parameter α is discussed below.

The one-electron effective Schrödinger equation which follows from (2.1) by application of the variational principle is

$$\Big[-\nabla_1^2+\sum_{\mu} g_{1\mu}+\int d\vec{r}_2\, g_{12}\,\rho(2) - 6\alpha\,\big((3/8\pi)\rho(1)\big)^{1/3}\Big]\,u_i(1)=\epsilon_i u_i(1)\ , \tag{2.9}$$

with solution by iteration to self-consistency being customary. The relation of the ϵ_i to $\langle E_{X\alpha}\rangle$ is such that the minimum total energy of the system is obtained by choosing the n_i in accord to Fermi statistics (see Ref. 29a for details).

The static lattice cohesive energy per particle at a unit cell volume V is then defined, for a monatomic solid, as

$$E(V)=\langle E_{X\alpha}(V)\rangle_{\mathrm{solid}}/N-\langle E_{X\alpha}\rangle_{\mathrm{atom}} \tag{2.10}$$

where the subscript solid indicates the value for the periodic volume in question, N is the number of atoms in that volume, and the subscript atom indicates the value for the isolated atom. It is understood in Eq. (2.10) that both terms on the right-hand side are calculated with the same value of α. [Note that Eq. (2.10) is the negative of the "cohesion" employed in Ref. 31.]. The minimum value of $E(V)$ will be quoted as the calculated value of the cohesive energy, with the corresponding value of a, the lattice constant, as the calculated equilibrium lattice constant.

The zero-temperature PV relation can be obtained from the model by two procedures which are analytically equivalent but computationally distinct. The first is the direct application of the thermodynamic definition of pressure to the $X\alpha$ total energy (2.1):

$$P=-\frac{d\langle E_{X\alpha}\rangle}{dV}\ . \tag{2.11}$$

Computational utilization of this expression involves numerical differentiation of a tabular function and consequent well-known loss of precision. An alternative procedure is to appeal to the virial theorem[29a]

$$PV=\tfrac{1}{3}\left[2\langle T_{X\alpha}\rangle+\langle W_{X\alpha}\rangle\right]\ , \tag{2.12}$$

which eliminates the numerical differentiation at the cost of using $\langle T_{X\alpha}\rangle$ and $\langle W_{X\alpha}\rangle$ separately. On account of the variation principle, these latter quantities are determined to lower order of precision than is $\langle E_{X\alpha}\rangle$. The relative merits of Eqs. (2.11) and (2.12) have been discussed, for example, by Löwdin.[40] For convenience we have uniformly employed Eq. (2.12) in the work reported here.

The selection of a value for α (the only disposable parameter in the model) has been the subject of much investigation and discussion.[29] One fairly common choice is α_{HF}: the value of α for which $\langle E_{X\alpha}\rangle_{\mathrm{atom}}$ is equal the Hartree-Fock total energy for the isolated atom. Since it is reasonably well established[41] that the Hartree-Fock treatment of a van der Waals system yields a purely repulsive interaction, the adjustment of α to yield a separated-atom limit which is identical (in total energy) to the Hartree-Fock atomic limit seems unlikely to be the most propitious procedure. The alternative which we have selected divorces the calculation from the Hartree-Fock atom, for we have employed what is usually called α_{VT}. This is the value that results from requiring

$$\langle E_{X\alpha}\rangle_{\mathrm{atom}}=\langle E_{\mathrm{SD}\alpha}\rangle_{\mathrm{atom}} \tag{2.13}$$

Here the subscript SDα indicates that the expectation of the exact many-electron Hamiltonian is with respect to a single determinant of the occupied $X\alpha$ orbitals. Equation (2.13) is equivalent to requiring (for the isolated atom)

$$2\langle T_{\mathrm{SD}\alpha}\rangle/\langle V_{\mathrm{SD}\alpha}\rangle=-1\ , \tag{2.14}$$

where T and V are the exact total kinetic and potential energy operators. Equation (2.14) gives the origin of the nomenclature α_{VT}, since that relation is just the virial theorem for the SDα wave function. Presumably the SDα determinant would dominate in a configuration-interaction (CI) expansion based on the $X\alpha$ orbitals, if, as has been conjectured,[42] the latter are reasonable facsimiles of the natural spin orbitals.[14] If this suggestion is correct the use of α_{VT} amounts to requiring that $\langle E_{X\alpha}\rangle$ be equal to the leading contribution from the CI expansion of the atomic ground state. If not, then the use of α_{VT} is at least a pragmatic way to construct a simple many-electron wave function from the $X\alpha$ orbitals which describes the isolated atom in a physically sensible way [i.e., Eq. (2.14) is satisfied].

The values of α_{VT} which we have used throughout this work are given in Table I. For Ar and Kr these are taken from Schwarz,[43] while the value for Xe was obtained by us using the same procedures as did Schwarz. Some indication of the quality of the description of the isolated atom provided by this choice of α can be obtained by comparing the resulting atomic excitation energies to experiment. In Ar, we find $[E_{X\alpha}(3p^5\,4s^1)-E_{X\alpha}(3p^6\,4s^0)]=0.871835$ Ry. For comparison, the weighted mean over the experimentally observed[44] $3p^5\,4s^1$ levels gives $[E(3p^5\,4s^1)-E(3p^6\,4s^0)]=0.856383$ Ry. It should be noted that the $X\alpha$ result is, as indicated,

TABLE I. Values of α_{VT} used in the present calculations.

Ar	0.72131
Kr	0.70544
Xe	0.69962

the difference of the two total energies and does not in any way rely upon an attempt to interpret the $X\alpha$ eigenvalues via Koopmans's theorem. As has been oft discussed,[29a,29b] the $X\alpha$ eigenvalues for the system ground state cannot be interpreted in the same way as Hartree-Fock eigenvalues. We will return to this point in our discussion of the calculated energy bands.

Our calculational procedure for the solution of Eq. (2.9) in the crystal was the self-consistent augmented-plane-wave (APW) expansion method.[45] As a consequence of the very flat character of the bands and the large intervals separating them, we were almost always able to treat only the topmost occupied s and p bands as true band states without any discernible loss in precision. The lower states were calculated as atomiclike levels in the crystalline self-consistent muffin-tin potential. The band states were calculated at the equivalent of 32 uniformly spaced points in the first Brillouin zone. At each of these points $\vec{k}$ the expansion in $\vec{K}$ of the solution to Eq. (2.9) was truncated at $|\vec{k}+\vec{K}|^2 \leq 78 \times (\pi/a)^2$ (where a is the lattice constant), while the expansion in L was truncated at $L = 11$. On the basis of computational experience (for Ar) with larger truncations, we estimate the numerical precision of the present calculation to be about ± 0.0002 Ry in the cohesive energy for Ar and ± 0.003 Ry in Xe (i.e., about two parts in 10^7 in total energy). The corresponding numerical precision in the calculated pressures is of the order of 8–10%. The computer code used was that previously employed by Averill,[31] which has been checked against the independently developed code used by Perrot. For Li with $\alpha = \frac{2}{3}$ both codes yield a cohesive energy[31,46] of -0.1236 Ry, a gratifying indication of reliability. The isolated atom calculations were made using a shortened version of the Herman-Skillman code.[47] All computations (both crystalline and atomic) used the Herman-Skillman radial mesh. Double-precision arithmetic was used exclusively. The calculations were performed on the IBM 360/65 and 370/165 machines of the University of Florida.

III. COHESIVE ENERGIES, PV RELATIONS

In Figs. 1–4 we present plots of our calculated E-vs-V results. In all these figures the curve connecting the calculated points is only a plausible "guide for the eye." It will be noted in Fig. 1 that Ar has separated to the (calculational) atomic limit at $V = 2000$ a.u.^{3} [a.u.^{3} = (bohr radius)^3], corresponding to $a = 20$ a.u. = 10.584 Å. Thus, $E(a = 20\text{ a.u.}) = 0.0000 \pm 0.0002$ Ry, so that the shape of $E(a)$ for large a is quite likely to be unreliable. In Table II we compare our calculated equilibrium E and a with the "experimental" static lattice values. The static lattice cohesive energies were obtained from the experimental values given by Pollack[48] by inclusion of the estimated zero-point energies tabulated by him.[49] Each of the calculated equilibrium cohesive energies in Table II corresponds to that value of a for which we were able to obtain the lowest (in magnitude) calculated pressure. In all cases, this calculated pressure was ≤ 1 kbar. The calculated values of a shown in Table II were obtained by interpolation of the calculated PV data to $P = 0$.

Perhaps the most obvious remark to be made about the data exhibited in Table II is that the model does exhibit binding of the proper order of magnitude and something like the proper dependence on Z. That the calculated Z dependence of E is too weak is to some extent misleading, for the numerical precision of the calculation also de-

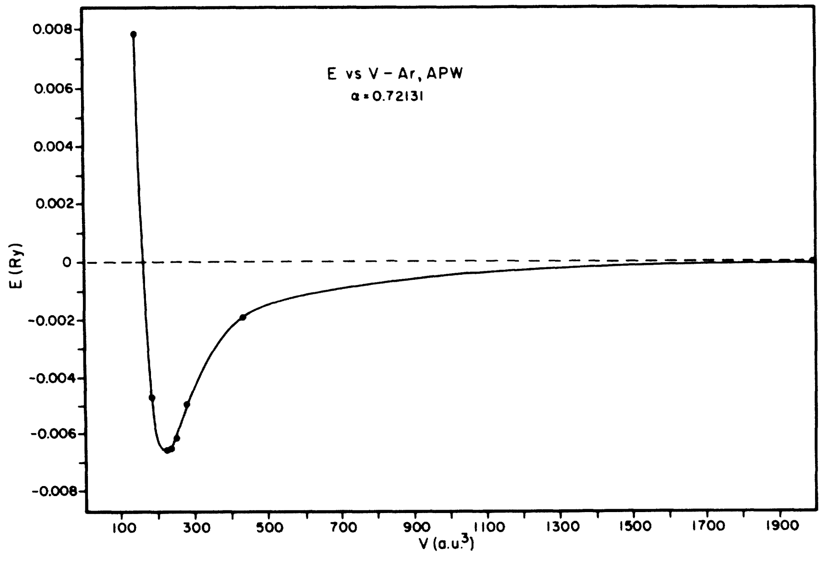

FIG. 1. Cohesive energy of fcc Ar as calculated in the range of unit cell volumes 182.25 → 2000 cubic atomic units, inclusive.

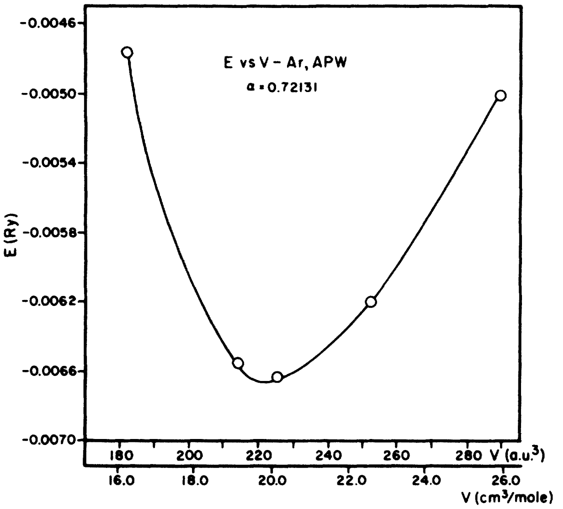

FIG. 2. Cohesive energy of fcc Ar as calculated in the "bowl" region.

creases with Z. Application of our precision estimate (recall Sec. II) of 2 parts in 10^7 of total energy gives numerical uncertainties of 0.0002 Ry for Ar (total energy ≈ 1050 Ry), 0.001 Ry for Kr (total energy ≈ 5500 Ry), and 0.003 Ry in Xe (total energy ≈ 14 500 Ry). As a distinctly secondary consideration we note that the error bars given for the Xe latent heat of sublimation at $T = 0$ K may be unrealistically small. Thus, Dobbs and Jones[50] report $L_{\mathrm{Xe}} = 3830 \pm 50$ cal/mole on the basis of work by Clusius and Weigand[51] and Whalley and Schneider.[52] However, the value given in Ref. 52 (and quoted in Ref. 48) is 3828 cal/mole, with no specified uncertainty. By comparison, L_{Ar} is reported in Ref. 50 as 1850 ± 12 cal/mole and in Ref. 52 as 1878 ± 40 cal/mole. It may be that a 2% or larger uncertainty should be applied to L_{Xe} just as for L_{Ar} in Ref. 52, particularly since L_{Xe} is obtained by extrapolation from the latent heat of vaporization at boiling (≈ 165 K).

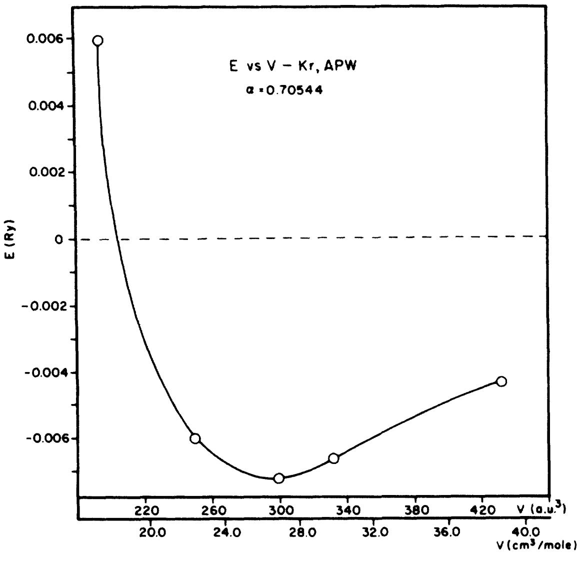

FIG. 3. Calculated cohesive energy for fcc Kr.

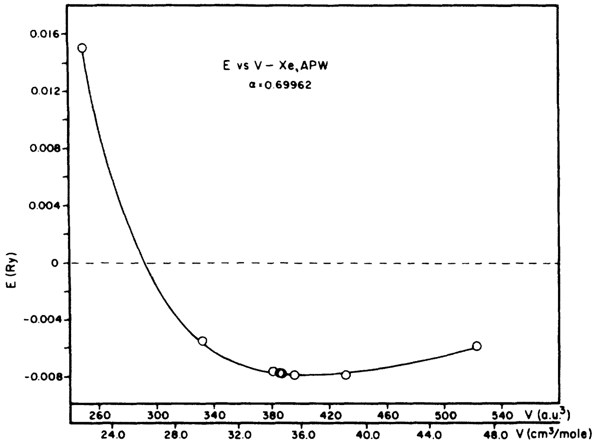

FIG. 4. Calculated cohesive energy for fcc Xe.

The effect of the choice of α upon the calculated cohesive energy may be illustrated by considering the effect of choosing the "Kohn-Sham-Gaspar" value $\alpha = \frac{2}{3}$.[29b] For Ar at $a = 10.039$ a.u. we find $E(\alpha = \frac{2}{3}) = -0.0053$ Ry/particle, an underbinding of 20%. The use of the Kohn-Sham-Gaspar choice of α would lead to results in much poorer accord with the empirical binding energies than those displayed in Table II, since past calculational experience[31] with the APW-$X\alpha$ method indicates that the lessened binding found for Ar with $\alpha = \frac{2}{3}$ would also occur to about the same degree for Kr and Xe.

In Figs. 5–8 we display the computed PV relations. For the positive pressures we have computed relevant P and V results. These are tabulated in Table III, along with the experimental quantities as obtained from the empirical Birch-Murnaghan equation of state obtained by Stewart.[53] The empirical pressures listed for Ar differ from those we quoted earlier[39] because of an error in reading Stewart's graphical 0–K isotherm. The Xe experimental Birch-Murnaghan parameters are attributed by Stewart to Packard and Swenson.[54] In either case, the raw experimental data were obtained from piston displacement measurements in the range $0 < P \leq 20$ kbar. As is well known,[53–55] such measurements present a number of severe technical problems and attendant errors. Notable among these are frictional errors (both sample and apparatus), calibration errors (due to large thermal gradients between the piston and the device

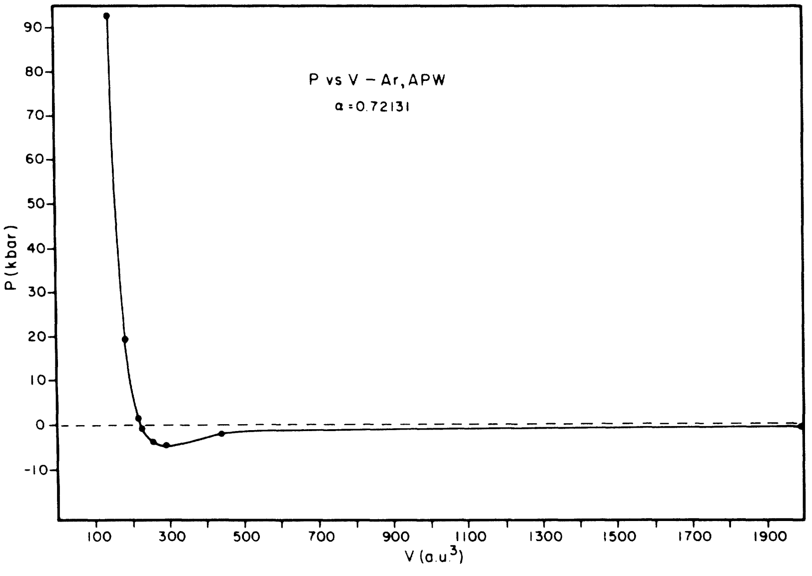

FIG. 5. Calculated *PV* relation (from the virial theorem) for fcc Ar, over the same volume range as Fig. 1.

measuring its displacement), and errors resulting from the requisite extrapolation to $P = 0$. As we have noted (recall Sec. II) the numerical precision of the present calculations is about 10% in the pressure. In view of the problems of precision presented by both the calculations and the experiments we view the comparison given in Table III as acceptable.

IV. EFFECTIVE PAIR POTENTIALS

It is not novel[56] to remark that the microscopic theory of the lattice dynamics of insulators is in a less-than-desirable state of development, at least so far as computational tractability is concerned. As a rather poor, temporary substitute for such a calculation, we may ask whether the cal-

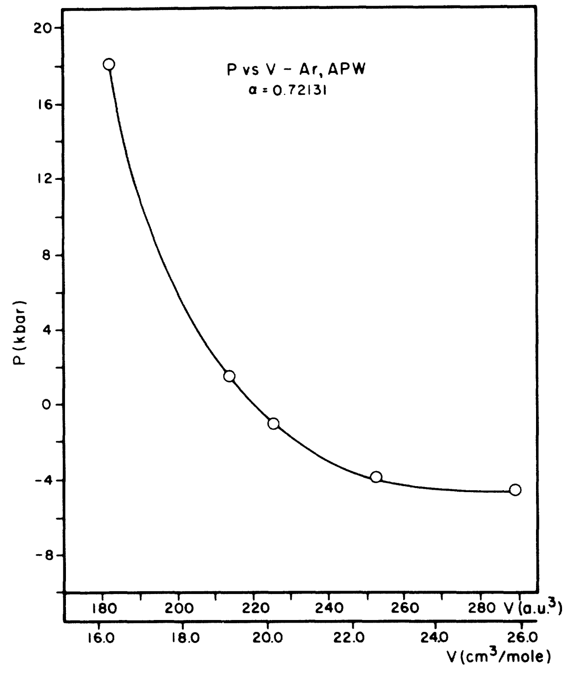

FIG. 6. Detail of calculated Ar *PV* relation corresponding to Fig. 2.

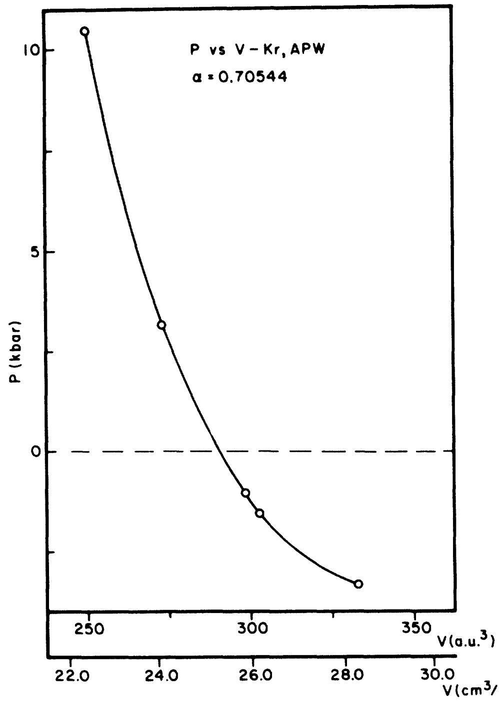

FIG. 7. Calculated *PV* relation for fcc Kr.

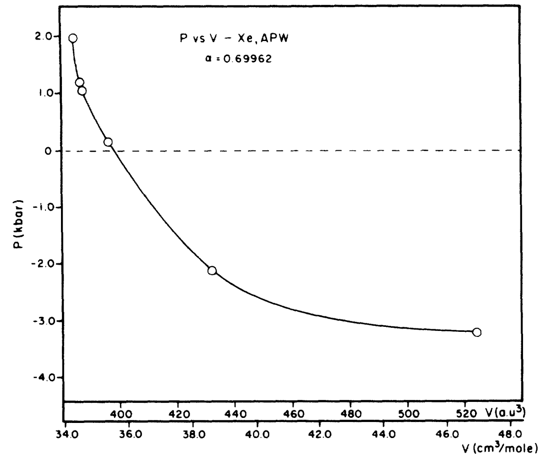

FIG. 8. Calculated *PV* relation for fcc Xe.

TABLE II. Calculated and experimental cohesive energies and interpolated equilibrium lattice constants.

	E (Ry/particle)		a (a.u.)	
	Expt.[a]	Calc.[b]	Expt.[a]	Calc.[c]
Ar	-0.00648	-0.00664 (9.668)	10.038	9.599
Kr	-0.00896	-0.00727 (10.61)	10.666	10.507
Xe	-0.01259	-0.00812 (11.66)	11.586	11.677

[a] See Ref. 48.

[b] Calculated at the lattice constant in a.u. shown in parentheses. This value corresponds to the lattice constant at which the most binding was actually computed and *not* to the interpolated calculated equilibrium lattice constant. See text regarding numerical uncertainties.

[c] Value from interpolation of calculated P-vs-V curve for $P=0$.

culated static lattice energies $E(V)$ determine a "reasonable" pair potential. That is, we assume an interatomic potential v_{ij} which contains core radius, well depth, etc., parameters. We then invoke the Born-Oppenheimer approximation[57] to require that

$$E(V)=\frac{1}{2N}\sum_{i=2}^{N} v_{1i} \tag{4.1}$$

for all V with the particles at their corresponding lattice sites. Since the assumed functional form for v_{ij} cannot be exact (because of the omission of three-body, four-body, etc., forces), we vary the parameters in v_{ij} until the lattice sum in Eq. (4.1) is closest, in a nonlinear-least-squares sense, to the APW-$X\alpha$ $E(V)$ data.

In Table IV we give the results of this procedure for a few simple potential functions, with empirically determined parameters for comparison. The empirical parameters for the Ar "exp-6-8" potential were obtained by least-squares fit of lattice sums of that potential to lattice sums of the Barker-Bobetic pair potential,[58] including the triple dipole interactions. The previously discussed deficiencies of the calculated $E(V)$ show up in these data in obvious ways. For example, the inadequate well depths for Kr and especially Xe are direct consequences of the underbinding in evidence in Table II. The fact that the shape of $E(V)$ for Xe is physically realistic (which follows immediately from the agreement of the calculated and empirical PV relations, see Table III) suggests that a rigid shift downward of $E(V)$ to match the empirical static lattice cohesive energy would result in a significant improvement in the potential parameters and such is the case. For the Lennard-Jones (LJ) potential, a downward shift of all the calculated Xe energies by 694.7 K (= 0.0044 Ry) results in fitted potential parameters of $\sigma = 3.965$ Å, $\epsilon = 222.88$ K.

The results given in Table IV also illuminate some deficiencies of the calculated $E(V)$ which are not obvious by direct inspection. For example, the coefficient c in the "exp-6-8" potential for Ar is determined by the present calculation to be positive, a clearly unphysical result which suggests that the calculated $E(V)$ goes to zero too rapidly, with increasing V. The same difficulty is hidden in the calculated LJ parameters. The assumed potential form relates long and short range behavior in a very rigid and inflexible way and the result is a seemingly good set of parameters but very high standard deviations with respect to the calculated $E(V)$. For Ar, Kr, and Xe those standard deviations for the LJ potential are, in order, 88.3, 63.5, and 56.6 K, values which are noticeably larger than the precision of the corresponding numerical $E(V)$ data. A major contribution to these large standard deviations occurs in the re-

TABLE III. Calculated and experimental pressures for various ratios of the volume V to the equilibrium volume V_0.

	$\frac{V}{V_0}$	P(kbar)	
		Calc.	Expt.[a]
Ar.	0.969	1.55	0.85
	0.824	18.17	10.06
	0.646	92.68	70.87
Kr	0.942	3.19	2.26
	0.862	10.46	8.17
	0.671	65.16	75.27
Xe	0.996	0.14	0.17
	0.955	1.95	2.04
	0.936	11.99	12.60
	0.628	78.57	102.12

[a] Reference 53.

TABLE IV. Parameters for some simple pair potentials, as determined by least-squares fit to APW-$X\alpha$ static lattice energies.

$\mathcal{V}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$; "Lennard-Jones"

	Ar		Kr		Xe	
	Expt.[a]	Calc.	Expt.[a]	Calc.	Expt.[a]	Calc.
σ(Å)	3.400	3.722 ±0.008	3.635	4.086 ±0.006	3.960	4.548 ±0.004
ϵ(K)	119.4	117.1 ±4.8	164.7	130.2 ±3.2	231.5	143.8 ±2.5

$\mathcal{V}(r) = \epsilon\{\exp[2a(r/r_0 - 1)] - 2\exp[a(r/r_0 - 1)]\}$; "Morse"

	Ar		Kr		Xe	
	Expt.[b]	Calc.	Expt.[b]	Calc.	Expt.[b]	Calc.
r_0(Å)	3.7793	3.616 ±0.011	4.0294	3.971 ±0.009	4.3984	4.430 ±0.017
ϵ (K)	149.1	158.8 ±2.2	208.7	174.2 ±1.4	288.5	189.4 ±2.20
a	−6.05	−6.866 ±0.103	−6.21	−6.866 ±0.078	−5.98	−6.805 ±0.119

$\mathcal{V}(r) = \exp[a(r-b)] + cr^{-6} + dr^{-8}$; "exp-6-8"

	Ar	
	Expt.[c]	Calc.
a(Å^{-1})	−3.832 ±0.005	−3.425 ±0.039
b(Å)	4.994 ±0.035	5.438 ±0.048
c(KÅ^6)	−5.84(±0.34) ×10^5	9.01(±1.26) ×10^5
d(KÅ^8)	−1.28(±0.85) ×10^6	−3.21(±0.32) ×10^7

[a] G. G. Chell and I. J. Zucker, J. Phys. C 1, 35 (1968).

[b] Reference 12, Table II.

[c] See text.

gion beyond the minimum, where a lattice sum of LJ potentials tends to zero much more slowly than the APW $E(V)$ it is being forced to fit. These difficulties in examining the large r behavior are aggravated by the fact that for the lattice constant in Ar, for example, at which a lattice sum of the best available pair potential is dominated by the r^{-6} behavior, the corresponding static lattice energy is smaller than the numerical precision of our calculations. Thus, we can only say that our calculated $E(V)$ data go to zero with increasing V faster than predicted by the best pair potential *for that range of* V for which the pure van der Waals attraction is not dominant.

The deficiencies just enumerated no doubt arise in part from the inherent limitations of our procedure. That is, even if the $X\alpha$ method were to provide a completely acceptable description of the rare-gas interaction (which we most emphatically do not claim), the recipe we have used is restricted to pair potentials in a cubically symmetric system. The unsatisfactory nature of the restriction to pairwise additivity has long been known for the alkali halides[14] and a subject of considerable discussion for the rare-gas crystals.[58] The cubic symmetry constraint is clearly energetically unfavorable at low densities, since it precludes a phase transition to a less ordered system. Nevertheless, it seems clear from Table IV that, particularly in the case of the Morse potentials, the APW-$X\alpha$ model gives pair potentials which are not unreasonable.

V. ONE-ELECTRON PROPERTIES

Perhaps the most often quoted "figure of merit" for an energy band calculation is the direct band gap. By now it is well known[29b] that the virtual Bloch levels calculated in the $X\alpha$ model do not, in the case of an insulator, correspond to the physical conduction band levels. That is, the $X\alpha$ scheme is a model of the insulator ground state. It is no surprise, therefore, that the calculated direct band gap for Ar ($\Gamma_{15} - \Gamma_1$) is 0.607 Ry at $a = 10.039$ a.u. (the experimental lattice constant), 0.6145 Ry at $a = 9.66773$ a.u. (the calculation nearest the calculated equilibrium lattice constant, recall Table II), and 0.642 Ry at $a = 9.00$ a.u. (substantially inside the calculated equilibrium value), in comparison with an experimental value of 1.05 Ry.[59] Boring[28] has found similar behavior for the Kr band gap.

More to the point are the calculated bandwidths for the "valence" states (Ar, 3s and 3p; Kr, 4s and 4p; Xe, 5s and 5p). Since all the other extant calculations have been at the relevant experimental lattice constant, we show in Table V our bandwidths at both the calculated and experimental value of a. In both Ar and Kr, the present calculation yields a valence s band that is discernibly narrower than the Hartree-Fock calculations; no such comparison is available for Xe but we have no reason to believe that similar results would not hold. The much older non-self-consistent $\alpha = 1$ statistical exchange calculations disagree among themselves in the case of the Ar 3s band, while the only similar calcula-

TABLE V. Valence-band widths (Ry). See text for comparisons with other calculations.

Ar	$3s$	$3p$
This calc. (a_{expt})	0.020	0.095
This calc. (a_{calc})	0.028	0.121
Statistical exchange[a]	0.010	0.046
Statistical exchange[b]	0.010	0.044
Statistical exchange[c]	0.022	0.145
Hartree-Fock exchange[d]	···	0.169
Hartree-Fock exchange[e]	···	0.089
Hartree-Fock exchange[f]	0.039	0.195
Kr	$4s$	$4p$
This calc. (a_{expt})	0.022	0.116
This calc. (a_{calc})	0.023	0.120
Statistical exchange[g]	0.022	0.092
Hartree-Fock exchange[h]	0.033	0.208
Xe	$5s$	$5p$
This calc. (a_{expt})[i]	0.033	0.136
This calc. (a_{calc})	0.031	0.130
Statistical exchange[j]	0.022	0.087

[a] Reference 16.
[b] Reference 17.
[c] Reference 20.
[d] Reference 19. Includes correlation corrections.
[e] Reference 22.
[f] Reference 23.
[g] Reference 25. Measured from figure.
[h] Reference 16.
[i] The $4d$ bandwidth is 0.00001 Ry.
[j] Reference 27. Measured from figure. The statistical exchange used is somewhat different from the $X\alpha$ form.

tion for the Kr $4s$ band is in agreement with our result. The Ar $3p$ band is another story entirely, with calculated band widths in the literature all the way from 0.044 to 0.195 Ry. In our opinion, the earlier statistical exchange results can be ignored because of their lack of self-consistency and their employment of $\alpha = 1$. We believe that the very broad $3p$ bandwidths reported in Refs. 19 and 23 have been adequately explained by Rössler[18] (and confirmed by Dagens and Perrot[22]) as a consequence of poor convergence on the p-like states.[60] Dagens and Perrot[22] compared their $3p$ bandwidth (0.089 Ry) with that of Mattheiss[17] (0.049 Ry) and concluded that the difference was as should be expected on the basis of the general relationship between the Hartree-Fock and statistical exchange-correlation schemes. Our results do not support this interpretation, since for the same lattice constant we find a $3p$ bandwidth (0.095 Ry) almost identical with theirs. Clearly, our utilization of an "optimized atom" value of α (rather than $\alpha = 1$) and of self-consistency has played some role, as has their lack of iteration to self-consistency. The relative importance of these factors is, at this point, indeterminable.

VI. LIMITATIONS AND IMPROVEMENTS

The calculations which we have presented suffer, in spite of their striking degree of success, from several deficiencies and limitations. First, there are the restrictions which are inherent in the model: the omission of relativistic corrections and the lack of a well defined relationship between the exact system total energy and the assumed $X\alpha$ total energy [Eqs. (2.1)–(2.8)]. As to the former, one may hope that the relativistic corrections for the rare gas solid and the isolated rare-gas atom are nearly identical and hence are essentially cancelled by the subtraction used to find the cohesive energy. At present there exists, to our knowledge, no firm evidence as to the validity of this conjecture. As to the latter, there has been much discussion[61] of the degree to which the $X\alpha$ method treats electron-electron correlation and it seems safest to say that this is at present an unresolved controversy. Niebel and Venables[62] claim to have proved that the $X\alpha$ method cannot, in principle, contain van der Waals forces, but their proof appears to us to rest on the assumption that $X\alpha$ energy band theory is necessarily single determinant theory. We contend that this assumption is not at all obvious, since there exist many "single-particle" theories (e.g., t-matrix theories, theories incorporating Jastrow product wave functions, etc.) in which correlation effects are introduced in the single-particle Schrödinger equation via an effective potential.

The second way in which this calculation is limited is technical. We have employed the APW method in its classical form, that is, with the muffin-tin potential. Furthermore, the self-consistency iterations have been performed via the conventional but little-discussed "muffin-tin-charge" approximation.[45] An obvious first improvement over the present calculation would be to incorporate the non-muffin-tin charge in a fashion analogous to that devised by Connolly and Danese[38] for the "multiple-scattering-$X\alpha$" treatment of molecules. A second, more difficult improvement would be the removal of the muffin-tin approximation completely. A substantial number of efforts in this direction have been made.[63] There are at least two draw backs to these schemes: (1) at this point there seems to be no clear way to decide which is best; (ii) all of them involve a major increase in program complexity and operating cost relative to the extant muffin-tin codes.

In assessing the results that we have presented we note first that the calculated cohesive energy appears to have too weak a dependence on atomic number. That is, $\partial E/\partial Z$ is too positive. Interestingly, Averill's results on the alkali metals[31] may also be characterized by the statement that $\partial E/\partial Z$ is too positive, though this may be misleading, since he found too *strong* a Z dependence. One is tempted to conjecture, using the Z^4 dependence of spin-orbit splitting as a guide, that this problem stems from the neglect of relativistic corrections, but we are unaware of any formal or numerical evidence along these lines. Secondly, we note that our present numerical techniques are utterly incapable of coming to grips with the question of the relative stability of the fcc and hcp phases of solid Ar. The energy difference involved is about 7 μRy.[20] Even if the $X\alpha$ model is sufficiently realistic to account for the stabilization energy in principle, we would have to improve our numerical precision by two to three orders of magnitude to be able to undertake this calculation. Such an improvement is presently (and for the foreseeable future) beyond our reach. Third, as already noted, the interatomic potentials extracted from our calculations reflect both the shortcomings of the computed $E(V)$ values as well as the restrictions to pair potentials and cubic symmetry.

Despite the shortcomings just enumerated we believe that the work reported here is a useful first step toward our eventual goal of a truly first-principles treatment of both the electronic and lattice dynamical properties of the RGC. Within the bounds of numerical precision, the calculated cohesive energies, lattice parameters, and PV relations are all in reasonable agreement with experiment. In many instances the agreement is far more favorable. The extracted pair potentials, while not competitive in quality with those obtained by a direct computational effort, stand in at least a semiquantitative relation to the best available potentials. Both non-muffin-tin and relativistic corrections are within the realm of calculational feasibility and, when accomplished, should provide a significant insight into the extent of the validity of the present work

ACKNOWLEDGMENTS

We are grateful to many co-workers and other professional colleagues for valuable correspondence and/or conversation. In particular, we thank A. M. Boring, E. Boursey, J. B. Conklin, Jr., J. W. D. Connolly, L. Kleinman, D. D. Konowalow, J. Linderberg, K. Niebel, P.-O. Löwdin, F. Perrot, R. O. Simmons, J. C. Slater, and J. A. Venables. A significant portion of the computational costs for this work was borne by the North East Regional Data Center of the State University System of Florida.

[†] Supported in part by the National Science Foundation.

[1] F. London, Z. Phys. Chem. B **11**, 222 (1930).

[2] W. E. Bleick and J. E. Mayer, J. Chem. Phys. **2**, 252 (1934).

[3] V. Deitz, J. Franklin Inst. **219**, 459 (1935).

[4] For an accessible summary of the work of Ref. 1–3, see F. Seitz, *The Modern Theory of Solids* (Wiley, New York, 1940), Secs. 58 and 88.

[5] The references to this subject are so extensive as to render a complete listing impossible. In Ref. 6–12 we give a modest sample of the work since 1968. For work prior to that time see the references in G. K. Horton, Am. J. Phys. **36**, 93 (1968).

[6] J. A. Barker, M. V. Bobetic, and M. L. Klein, Phys. Lett. A **34**, 175 (1971), and references contained therein.

[7] M. L. Klein and W. G. Hoover, Phys. Rev. B **4**, 539 (1971), and references contained therein.

[8] I. J. Zucker and M. B. Doran, J. Phys. C **5**, 2302 (1972), and references contained therein.

[9] G. L. Pollack, Phys. Rev. A **2**, 38 (1970), and references contained therein.

[10] J. B. Burton, Chem. Phys. Lett. **5**, 312 (1970), and references contained therein.

[11] G. E. Jelinek, Phys. Rev. B **5**, 3210 (1972), and references contained therein.

[12] H. R. Glyde, J. Phys. C **3**, 810 (1970).

[13] J. Linderberg and F. W. Bystrand, Ark. Fys. **26**, 383 (1964).

[14] P.-O. Löwdin, Adv. Phys. **5**, 1 (1956).

[15] J. Linderberg, Ark. Fys. **26**, 323 (1964).

[16] R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).

[17] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

[18] U. Rössler, Phys. Status Solidi **42**, 345 (1970).

[19] N. O. Lipari and W. B. Fowler, Phys. Rev. B **2**, 3354 (1970).

[20] R. Ramirez and L. M. Falicov, Phys. Rev. B **1**, 3464 (1970).

[21] A. B. Kunz, Phys. Status Solidi B **46**, 385 (1971).

[22] L. Dagens and F. Perrot, Phys. Rev. B **5**, 641 (1972).

[23] N. O. Lipari, Phys. Rev. B **6**, 4071 (1972).

[24] N. O. Lipari, Int. J. Quantum Chem. **6S**, 403 (1972).

[25] W. B. Fowler, Phys. Rev. **132**, 1591 (1963).

[26] N. O. Lipari, Phys. Status Solidi **40**, 691 (1970).

[27] M. H. Reilly, J. Phys. Chem. Solids **28**, 2067 (1967).

[28] A. M. Boring (private communication).

[29] Citations to local exchange theories are so extensive as to make a thorough biliography prohibitively lengthy. For detailed references the following should be consulted: (a) J. C. Slater, Adv. Quantum Chem. **6**, 1 (1972); (b) J. C. Slater and K. H. Johnson, Phys. Rev. B **5**, 844 (1972); (c) L. Hedin and S. Lundqvist, J. Phys. Colloque **C3**, C3-73 (1972).

[30] P. D. DeCicco, Phys. Rev. 153, 931 (1967).

[31] F. W. Averill, Phys. Rev. B **6**, 3637 (1972).

[32] W. E. Rudge, Phys. Rev. **181**, 1033 (1969).

[33] D. A. Liberman, Phys. Rev. B **3**, 2081 (1971).

[34] M. Ross and K. W. Johnson, Phys. Rev. B **2**, 4709 (1970).

[35] L. Kleinman and R. Shurtleff, Phys. Rev. B **4**, 3284 (1971).

[36] T. M. Hattox, J. B. Conklin, Jr., J. C. Slater, and S. B. Trickey, J. Phys. Chem. Solids. 34, 1627 (1973).

[37] D. D. Konowalow, P. Weinberger, J.-L. Calais, and J. W. D. Connolly, Chem. Phys. Lett. **16**, 81 (1972).

[38] J. W. D. Connolly and J. B. Danese (private communication).

[39] S. B. Trickey, F. W. Averill, and F. R. Green, Jr., Phys. Lett. A **41**, 385 (1972).

[40] P.-O. Löwdin, J. Mol. Spectrosc. **3**, 46 (1959).

[41] Neil Kestner, J. Chem. Phys. **48**, 252 (1968), and references contained therein.

[42] J. C. Slater (private communication).

[43] K. Schwarz, Phys. Rev. B **5**, 2466 (1972).

[44] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Circular No. 467 (U.S. GPO, Washington, D. C., 1949), Vol. I, p. 212.

[45] A. convenient review of the APW with references to the original literature is L. F. Mattheiss, J. H. Wood, and A. C. Switendick, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1968), Vol. 8, p. 63.

[46] F. Perrot (private communication).

[47] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[48] G. L. Pollack, Rev. Mod. Phys. **36**, 748 (1964), Table VIII.

[49] Note that the static-lattice values given here are corrected slightly from those we quoted in Ref. 39.

[50] E. R. Dobbs and G. O. Jones, Rep. Prog. Phys. **20**, 516 (1957).

[51] K. Clusius and K. Weigand, Z. Phys. Chem. B **46**, 1 (1940).

[52] E. Whaley and W. G. Schneider, J. Chem. Phys. **23**, 1644 (1955).

[53] J. W. Stewart, J. Phys. Chem. Solids **29**, 641 (1968).

[54] J. R. Packard and C. A. Swenson, J. Phys. Chem. Solids **24**, 1405 (1963).

[55] R. O. Simmons (private communication).

[56] For example, see R. M. Pick, in *Computational Solid State Physics*, edited by F. Herman, N. W. Dalton, and T. R. Koehler (Plenum, New York, 1972), p. 325.

[57] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. I, pp. 10–13 and Appendix 2.

[58] M. V. Bobetic and J. A. Barker, Phys. Rev. B **2**, 4169 (1970).

[59] G. Baldini, Phys. Rev. **128**, 1562 (1962). We note that Dagens and Perrot, Ref. 22, quote 1.038 Ry as the experimental gap but cite a reference which does not contain any information on the subject. Dr. E. Boursey has apparently resolved the confusion by pointing out to us the work of R. Haensel, G. Keitel, E. G. Koch, M. Skibowski, and P. Schreiber [Phys. Rev. Lett. **23**, 1160 (1969)] as the source for the value 1.0386 Ry.

[60] It may also be significant that Lipari and Fowler used a simple superposition of atomic statistical exchanges to calculate the crystalline statistical exchange, a procedure of dubious validity.

[61] See, for example, P. Jørgenson and N. Y. Öhrn, Phys. Rev. A. 8, 112 (1973); E. A. Kmetko, Bull. Am. Phys. Soc. 18, 455 (1973); A. R. Williams, J. F. Janak, and V. L. Moruzzi, Bull. Am. Phys. Soc. **18**, 457 (1973).

[62] K. Niebel and J. A. Venables (unpublished).

[63] For example, Ref. 30; L. Kleinman and R. Shurtleff, Phys. Rev. **188**, 1111 (1969); W. E. Rudge, Phys. Rev. **181**, 1024 (1969); E. O. Kane, Phys. Rev. B 4, 1971); and several others.