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Comparison of Theoretical and Experimental Charge Densities for C, Si, Ge, and ZnSe[†]

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Fourier transforms of the charge densities of C (diamond), Si, Ge, and ZnSe are calculated using the self-consistent orthogonalized-plane-wave (OPW) programs developed at the Aerospace Research Laboratory. Results obtained with the Slater, Kohn-Sham, and Liberman exchange approximations are compared with the most reliable experimental results and with previous theoretical results (obtained for diamond only). While the results are better than the free-atom form factors, there are still significant discrepancies between theoretical and experimental values.

I. INTRODUCTION

THE purpose of this paper is to present calculations of charge densities of C (diamond), Si, Ge, and ZnSe and to compare the results with the measured charge densities. To make this comparison, one needs first to assess the crystal x-ray scattering data to determine the most valid measurements. Then the theoretical results, which were obtained by using a self-consistent orthogonalized-plane-wave (SCOPW) model developed at the Aerospace Research Laboratories (ARL),[1] can be evaluated by comparison.

The SCOPW model was originally developed for the calculation of electron energy bands in crystals. Calculations have been performed[1–7] on C, Si,[2] Ge, ZnSe,[3] ZnS,[3] CdSe,[3] CdS,[1,3] GaAs,[4] GaP,[5] AlAs,[6] and AlP.[7] The calculated one-electron energy differences (band gaps, ϵ_2 peaks and conduction-band minima) have been compared with experiment, and the effects of various exchange approximations (Slater's,[8] Kohn and Sham's,[9] and Liberman's[10]) upon the band energies have been discussed.[11,12] It was found that the use of Slater's exchange potential for all the above crystals gives band energies in surprisingly close agreement with experiment, whereas for atomic systems, Liberman's approximation is the best of the three. Consequently, it is of interest to test results other than one-electron energies obtained by the SCOPW method, using the different exchange approximations. In particular, the Fourier transforms of the electron charge density, i.e., the x-ray form factors, have been investigated as functions of the exchange approximations.

Previous theoretical form-factor calculations for diamond have been performed by Kleinman and Phillips,[13] Bennemann,[14] Clark,[15] and Goroff and Kleinman.[16] While the earliest calculations involved the pseudopotential technique with all of its limitations, the calculation of Goroff and Kleinman is conceptually quite satisfactory. They used the orthogonalized-plane-wave (OPW) formalism with Slater's exchange and iterated the valence charge density to self-consistency. The core 1*s* wave function was not iterated, and the free-atomic wave function was used throughout the calculation. The core energy was adjusted, however, for the crystalline environment. They used a simplified method of Fourier transforming the exchange potential. Their charge density was averaged over six points (Γ, X, L, W, Σ, and Δ) in the Brillouin zone (see Fig. 1). They obtained remarkably close agreement with the experimental results. Therefore, it is of interest to compare the results of their model with those of the present model.

In Sec. II, we discuss the accuracy of the available experimental results and select those which in our judgment are the best. The theoretical SCOPW model is briefly outlined in Sec. III. Particular attention is paid to the convergence of the results with respect to the number of OPW's used in the calculation and with respect to the number of points used in averaging the charge density over the Brillouin zone. Section IV presents the theoretical results and compares them with

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the previous calculations for diamond and with the best experimental data. Section V then summarizes the findings of the paper.

II. EXPERIMENTAL SITUATION

The magnitude of the Fourier components of the charge distribution can be measured by x-ray diffraction from ideally perfect or ideally imperfect crystals. The formalism is different in the two cases, as are the scattering processes involved. The difficulty is to establish unambiguously that a particular sample represents one of the two ideal cases. This is particularly important since most crystals, although clearly imperfect, are not completely so, and a departure from the ideal mosaic arrangement results in a decrease of the amplitude of the scattered wave (extinction). This effect, when small, can easily be mistaken for a crystal-field effect, since it primarily affects the first intense lines, to which the contribution of the outer electrons is greatest.

A. Powder Case

Attempts to obtain ideally imperfect samples by using cold-worked powders,[17] where mechanical strains should yield an ideal mosaic, have been mildly successful. Although the x-ray measurement is in principle straightforward, the number of parameters to be carefully controlled is too large to permit high accuracy, simply because of the accumulation of partial errors. Sample preparation becomes a crucial problem, and in many cases it is simply impossible to obtain samples free of extinction, porosity, surface roughness, and preferred orientation, to cite only a few of the possible sources of error. At this time the highest degree of accuracy, attainable only in a few optimal cases, appears to be ±1.0% on the first few structure factors. At larger angles the uncertainty in quantities, such as the Debye temperature, the thermal diffuse scattering, and the polarizing properties of the monochromating crystal, reduces the accuracy to the 3–5% range. Furthermore, it is not clear that we fully understand all the parameters influencing the experiment at the level of a few tenths of a percent.

All of these difficulties should be kept in mind as one compares the published results with a theoretical model. However, it is important to realize that with all their shortcomings the powder measurements have yielded valuable, though limited, quantitative information. In particular, they have shown the spreading out of the outer electrons in the case of many simple metals. This has been thoroughly discussed by Weiss,[18] especially from the point of view of comparing the powder results with perfect-crystal results in the case of Cu,[19] and with imperfect-crystal results carefully corrected for secondary extinction, in the case of Al[20] and Fe.[21] The agreement between these various experiments is satisfactory. In general, the observed structure factors agree with the free-atom relativistic Hartree-Fock calculation (RHF) for the high-order peaks,[18] to which the major contribution comes from the closed-shell electrons, while they depart from the calculation for the first two peaks. For these, the structure factors are lower than the RHF values, suggesting a spreading out of the outer electrons. The picture has been further confirmed by recent work on powders, by transmission on Al[22] and by reflection on Al,[23,24] Cu,[25] and Ni.[26]

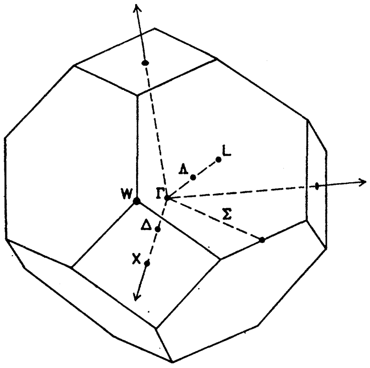

FIG. 1. Zinc-blende Brillouin zone, showing the following points: $\Gamma(0,0,0)$, $X(1,0,0)$, $L(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $W(1,0,\frac{1}{2})$, $\Delta(\frac{1}{2},0,0)$, $\Lambda(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, and $\Sigma(\frac{1}{2},\frac{1}{2},0)$.

These experiments on simple metals, however, are somewhat insensitive to a small redistribution of the outer electrons, since the largest contribution to the total scattering comes from the inner electrons, which are essentially unaffected by the crystal field. Structures of high symmetry and two kinds of atoms A and B have an interesting property that emphasizes the modification of the valence electron density. In the zinc-blende structure, for instance, the structure factor can be represented by

$$F(s)=f_A(s)+i^{h+k+l}f_B(s)\,, \tag{1}$$

with

$$f(s)=[f^\circ(s)+\Delta f'+i\Delta f'']\exp[-Ws^2]$$

and

$$s=|K|/4\pi\,,$$

where $f^\circ(s)$ is the free-atom form factor, hkl are the Miller indices or components of the scattering vector K, $\Delta f'$, and $\Delta f''$ are the real and imaginary parts of the

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TABLE I. Comparison of observed x-ray intensities for ZnSe with values calculated using optimal temperature factors $W_{Zn}=1.34$, $W_{Se}=0.68$.

hkl	2θ (deg)	Observed intensity	Calculated intensity	Ratio 100 (I_{obs}/I_{calc})
111	27.25	195983	195982	100.00
200 [a]	31.57	1567	1210	129.50
220	45.23	135351	138672	97.60
311	53.58	83934	81575	102.89
222 [a]	56.16	455	547	83.18
400	65.84	20821	21067	98.83
331	72.63	31064	31726	97.91
420 [a]	74.83	808	1252	64.54
422	83.46	38516	39999	96.29
440	100.38	12451	12451	100.00
531	106.93	23065	23064	100.00
620	118.41	20558	19885	103.38
622 [a]	128.58	725	1277	56.73
444	140.50	7534	7189	104.78

[a] Difference lines.

correction for anomalous dispersion, and W is a quantity proportional to the mean-square amplitude of vibration called the Debye-Waller factor.

Such a representation corresponds to a simple superposition of atomic charge densities. If $(h+k+l)$ is an even number not divisible by 4, the structure factor $F(s)$ is the difference between the scattering $f_A(s)$ of A and the scattering $f_B(s)$ of B. If A and B are in the same row of the Periodic Table, the core distributions will be very similar and largely cancel each other's contributions. The intensities of "difference lines" will then mostly reflect the differences in outer-electron distribution between A and B.

The results of a measurement performed on ZnSe powder[27] are presented in Table I. The calculated intensities have been obtained using the theoretical Hartree-Fock free-atom form factors and optimizing the scaling factor and the two temperature factors (W_{Zn} and W_{Se}) to fit the observed intensities. As can be seen by comparing the third and fourth columns of Table I, the intensities of difference lines are very far from the values calculated by Eq. (1), which represents a simple superposition of the neutral free atoms. Furthermore, the temperature factors W_{Zn} and W_{Se} are very different, which is improbable because the two atoms have very similar masses. A possible explanation for this is that the atoms have very different radii, that of Zn being much smaller. This would imply that the outer electrons have been redistributed, with some of them spending more time on the Se than on the Zn. This possibility has been investigated by assuming a distribution in real space for the electrons transferred. A number of different functional representations were used, such as

$$are^{-b|r|},\quad ar^2e^{-b|r|^2},\quad \text{and}\quad ae^{-b|r|^2},$$

which lead to various expressions for the structure factor. In the case of the Gaussian, for instance, one obtains the expression

$$F(hkl)=[f_{Zn}(hkl)-\alpha\exp-\beta_{Zn}s^2]\exp-W_{Zn}s^2 \\ +i^{h+k+l}[f_{Se}(hkl)+\alpha\exp-\beta_{Se}s^2]\exp-W_{Se}s^2,$$

where α, β_{Zn}, β_{Se}, W_{Zn}, and W_{Se} were determined from the experiment. The results for this case are presented in Table II; they are indistinguishable from those obtained using any of the other representations for the electron distribution. In all cases α, the parameter representing the total number of electrons transferred from Zn to Se, was found to be 0.7 ± 0.1, while W_{Zn} and W_{Se} converged to 0.97 ± 0.07 and 0.74 ± 0.01, respectively. The latter values show that, under the given hypothesis, the mean-square amplitudes of vibration, which are proportional to the W's, are no longer unacceptably different. Table II also shows convincingly that the discrepancies affecting the difference lines have disappeared while the fit to the other lines has not worsened. It follows that the model proposed can effectively represent the data. However, it is very phenomenological and therefore yields little more than a qualitative confirmation of the charge-transfer hypothesis. A more fundamental quantum-mechanical model would be submitted to a very stringent test on its ability to yield detailed wave functions. This is why these data for ZnSe, corrected for thermal vibrations using $W_{Zn}=0.97$ and $W_{Se}=0.74$, were chosen for a comparison with the SCOPW results discussed later.

B. Perfect-Crystal Case

The kinematical theory, which describes accurately the scattering processes in the ideal mosaic situation, does not apply to perfect crystals, where there is an interaction between the incident and diffracted beams. The perfect-crystal problem, which consists of solving the Maxwell equations for a medium with a periodic

TABLE II. Comparison of observed x-ray intensities for ZnSe with values calculated for Gaussian distribution of transferred electrons assuming for the parameters $W_{Zn}=0.9879$, $W_{Se}=0.7361$, $\alpha=0.71$, $\beta_{Zn}=11.45$, $\beta_{Se}=14.92$.

hkl	2θ (deg)	Observed intensity	Calculated intensity
111	27.25	195983	189606
200	31.57	1567	1567
220	45.23	135351	135224
311	53.58	83934	79969
222	56.16	455	454
400	65.84	20821	20849
331	72.63	31064	31354
420	74.83	808	854
422	83.46	38516	40131
440	100.38	12451	12644
531	106.93	23065	23064
620	118.41	20558	20424
622	128.58	725	725
444	140.50	7534	7458

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complex dielectric constant, has received a great deal of attention. The formalism developed is known as the "dynamic theory," and Batterman and Cole[28] have recently reviewed the subject.

The experimental procedures used[18] for measuring diffracted intensity are only slightly different from the powder case, and the sources of inaccuracy in the measurements proper are very similar. The errors due to the condition of the sample, on the other hand, are largely eliminated. Once the crystal's purity and "perfection" have been established, for example, by mass spectrography and Lang topography, the characterization is complete. Such effects as extinction, porosity, preferred orientation, and particle-size line broadening have no equivalent here. Perfect crystals, however, have been grown for very few materials, principally Ge and Si, on which Jennings[29] has recently performed high-accuracy measurements of diffracted intensity.

An alternative experimental method was developed by Kato and Lang,[30] who showed that a phenomenon predicted by the dynamic theory, the pendellösung effect, could be observed in perfect crystals and used to determine the structure factor. Here the errors are confined to the measurements of the wedge angle and the interfringe distance. This technique has been mostly applied to Si. The first extensive work was done by Hattori, Kuryiama, and Kato,[31] who obtained an accuracy of ±1.5% in the form factor. More recently Hart and Milne[32] have measured the 220 form factor with an accuracy of the order of ±0.4%.

The experimental form factors appearing to be the most dependable at this time are: for Si, the 111 and 222 measured by Jennings,[29] the 220 measured by Hart and Milne,[32] and all the other reflections measured by Hattori, Kuriyama, and Kato[31]; for Ge, the 111 measured by Jennings.[29] These results together with those of Götlicher and Wolfel[15] on diamond are used in Tables VII–X.

III. SCOPW MODEL

The SCOPW programs used to calculate the crystal structure factors have given surprisingly good one-electron band energies for numerous compounds with the diamond, zinc-blende, and wurtzite structures, as listed in the Introduction. For ZnS and Si, where relativity is not important, the unadjusted band energies fit all known experimental facts when Slater's exchange approximation[8] is used.

The basic Hamiltonian for the model is

$$H=-\tfrac{1}{2}\nabla^2+V_{\mathrm{Coul}}(r)-E_x 6[3\rho(r)/8\pi]^{1/3}.$$

Relativistic corrections are ignored. $V_{\mathrm{Coul}}(r)$ is the electron Coulomb potential energy resulting from all the charge in the crystal. $\rho(r)$ is the electron number density. The Hartree-Fock exchange term is approximated either by Slater's average exchange $E_x=1$; by Kohn and Sham's[9] minimization of the total energy of a free-electron gas $E_x=\frac{2}{3}$; or by Liberman's approximation[10] $E_x(r)=4/3f(k/k_F)$, in which

$$f(n)=\frac{1}{2}+\frac{1-n^2}{4n}\ln\left|\frac{1+n}{1-n}\right| .$$

The Fermi-Thomas model is used to obtain k and k_F. k_F, the Fermi energy, is $[3\pi^2\rho(r)]^{1/3}$, and k is $\{2m[E_n-V(r)]\}^{1/2}$, where E_n is the one-electron energy of the state being calculated.

In the OPW model,[33] the electronic states are divided into tightly bound core states and loosely bound valence states. The core states must have negligible overlap from atom to atom. They are calculated from a spherically symmetrized crystalline potential. The valence states must be well described by a modified Fourier series,

$$\Psi_{\mathbf{k}_0}(\mathbf{r})=\textstyle\sum_\mu B_\mu[(\Omega_0)^{-1/2}e^{i\mathbf{k}_\mu\cdot\mathbf{r}}$$
$$-\textstyle\sum_a e^{i\mathbf{k}_\mu\cdot\mathbf{R}_a}\sum_c A_{c\mu}{}^{\alpha}\psi_c(\mathbf{r}-\mathbf{R}_a)],\quad \mathbf{k}_\mu=\mathbf{k}_0+\mathbf{K}_\mu$$

where $\mathbf{k}_0$ locates the electron within the first Brillouin zone, $\mathbf{K}_\mu$ is a reciprocal-lattice vector, $\mathbf{r}_a$ is an atom location, Ψ_c is a core wave function, and Ω_0 is the volume of the crystal unit cell. The coefficients $A_{c\mu}{}^{a}$ are determined by requiring that $\Psi_{\mathbf{k}_0}(\mathbf{r})$ be orthogonal to all core-state wave functions. Variation of the B_μ to minimize the energy then results in the valence one-electron energies and wave functions.

The dual requirements of no appreciable core overlap and convergence of the valence wave-function expansion with a reasonable number of OPW's determine the division of electron states into core and valence states. The states taken as valence states are the $2s$ and $2p$ for diamond, $3s$ and $3p$ for Si, and $4s$ and $4p$ for Ge, Zn, and Se. Good convergence of the Fourier series is obtained with 229 OPW's.[1,3] The OPW convergence of ZnSe Slater structure factors is illustrated in Table III, where self-consistent results are given for 137 OPW's (at the Γ point and a comparable number at the other high-symmetry points) and for 229 OPW's. The differences are small—less than 0.07—and should indicate an upper limit to the error due to lack of OPW convergence.

The calculation is self-consistent in the sense that core and valence wave functions are calculated alternately until neither changes appreciably. The Coulomb potential due to the valence electrons and the valence charge density are both spherically symmetrized about

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TABLE III. Convergence of theoretical Slater structure factors for ZnSe with respect to the number of OPW's used in the valence wave-function expansion. Structure-factor units are electrons per crystallographic unit cell.

hkl	F_{137}[a]	F_{229}[b]
111	157.66	157.68
200	11.73	11.72
220	191.09	191.14
311	126.37	126.40
222	9.54	9.61
400	163.52	163.57
331	111.07	111.13
420	10.80	10.85

[a] For 137 OPW's.
[b] For 229 OPW's.

each inequivalent atom site. With these valence quantities frozen, new core wave functions are calculated and iterated until the core wave functions are mutually self-consistent. Modified Herman-Skillman[34] programs are used for the core wave-function calculation. Then the total electronic charge density is calculated at 506 crystal mesh points covering 1/24 of the unit cell, and the Fourier transform of $\rho(r)^{1/3}$ is taken. The new crystal potential is calculated from the old valence charge distribution and the new core charge distribution. New core-valence orthogonality coefficients $A_{c\mu}{}^{a}$ are calculated. The iteration cycle is then completed by the calculation of new valence energies and wave functions. The iteration process is continued until the valence one-electron energies change less than 0.01 eV from iteration to iteration. The form factors then fluctuate less than 0.03. For compounds such as ZnSe the procedure for incorporating Liberman's exchange is slightly different. It is discussed at length in another paper.[11]

The appropriate charge density to use for both the self-consistent potential calculation and the form-factor calculation is the average charge density of all the electrons in the Brillouin zone. For most of the self-consistent calculations presented here, this average is approximated by a weighted sum over electrons at the Γ, X, L, and W high-symmetry points of the Brillouin zone, shown in Fig. 1. The weights are proportional to the volumes within the first Brillouin zone closest to each high-symmetry point.[35] The adequacy of this approximation is illustrated for ZnSe, where separate self-consistent runs were made for each of several different zone averages. Table IV gives resulting three-, four-, and six-point self-consistent form factors. Table V gives the band energies for the three-, four-, and six-point iterations, as well as for iterations where only the Γ-point charge density or only the L-point charge density was used. Clearly the L-point charge density is much more representative of the zone as a whole than is the Γ-point charge density. This is not surprising since most of the electrons are in the outer regions of the zone. The valence-band energies change a maximum of 0.06 eV from four to six points, but the conduction-band energies change considerably more. The form factors change a maximum of 0.11 from four to six points. Clearly, convergence with respect to Brillouin-zone averaging is not complete even when six points are used, but the error in the calculated form factors is probably less than 0.20 for ZnSe when four-point results are used. Four- and six-point self-consistent runs were also made for diamond. The results, included in Table VI, again show almost complete convergence. The form factors quoted in the remainder of the paper will be four-point form factors unless otherwise noted.

TABLE IV. Theoretical Slater self-consistent structure factors for ZnSe. Structure-factor units are electrons per crystallographic unit cell. These structure factors were calculated by using three-, four-, and six-point averages over the Brillouin zone. Three-point weightings over Γ, X, and L are 0.125, 0.375, and 0.500. Four-point weightings over Γ, X, L, and W are 0.1258, 0.1731, 0.3600, and 0.3411. Six-point weightings over Γ, X, L, W, Δ, and Σ are 0.03125, 0.09375, 0.125, 0.1875, 0.1875, and 0.375. Self-consistency was obtained in each case.

		Structure factor	
hkl	Three-point	Four-point	Six-point
111	157.86	157.68	157.61
200	11.78	11.74	11.63
220	191.14	191.15	191.12
311	126.35	126.41	126.41
222	9.58	9.61	9.63
400	163.53	163.57	163.56
331	111.13	111.13	111.10
420	10.84	10.85	10.85

TABLE V. Theoretical band energies (relative to the Γ_{15v}) for ZnSe (Slater exchange) when Brillouin-zone averages were taken only at Γ, only at L, and over the three, four, and six points given with their weightings in the caption to Table IV. Self-consistency was obtained in each case. All energies are in eV.

	Γ	L	Three-point	Four-point	Six-point
Γ_{15c}	4.64	6.43	6.35	6.66	6.75
Γ_{1c}	1.65	2.75	2.70	2.94	3.01
Γ_{15v}	0	0	0	0	0
Γ_{1v}	−11.86	−11.83	−11.83	−11.82	−11.81
L_{1c}	9.65	9.57	9.68	9.72	9.78
L_{3c}	5.62	7.11	7.05	7.32	7.41
L_{1c}	2.08	3.59	3.51	3.79	3.88
L_{3v}	−0.91	−0.66	−0.67	−0.64	−0.63
L_{1v}	−5.72	−4.53	−4.57	−4.40	−4.34
L_{1v}	−10.46	−10.81	−10.80	−10.84	−10.85
X_{3c}			4.22	4.49	4.58
X_{1c}			4.00	4.19	4.28
X_{5v}			−1.72	−1.65	−1.63
X_{3v}			−4.51	−4.31	−4.25
X_{1v}			−10.42	−10.48	−10.50

The form factors are obtained in the following way. One can write the valence charge density as

$$\rho_{\mathrm{V}}(\mathbf{r}) = \rho_{\mathrm{PW}}(\mathbf{r}) + \rho_{\mathrm{V-c}}(\mathbf{r}),$$

where $\rho_{\mathrm{PW}}(r)$ contains the plane-wave–plane-wave terms and $\rho_{\mathrm{V-c}}(r)$ contains the terms involving the ortho-

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TABLE VI. Comparison of experimental and calculated structure factors for diamond. Structure-factor units are electrons per crystallographic unit cell.

hkl	Expt	RHF	S6[a]	S[b]	KS[c]	L[d]	S6-RHF[e]	S-RHF[e]	KS-RHF[f]	L-RHF[g]
111	3.32	3.03	3.30	3.33	3.23	3.19	3.30	3.33	3.23	3.19
220	1.98	1.96	1.95	1.97	1.92	1.88	1.95	1.97	1.93	1.89
311	1.66	1.76	1.66	1.66	1.64	1.61	1.65	1.65	1.65	1.61
222	0.14	0.00	0.12	0.14	0.12	0.14	0.12	0.14	0.12	0.14
400	1.48	1.59	1.53	1.53	1.52	1.51	1.52	1.52	1.53	1.52
331	1.58	1.52	1.53	1.55	1.52	1.53	1.53	1.55	1.54	1.53
422	1.42	1.44	1.41	1.42	1.40	1.41	1.40	1.41	1.41	1.42
511	1.42	1.40	1.37	1.37	1.35	1.36	1.36	1.36	1.36	1.37
333	1.42	1.40	1.34	1.34	1.32	1.33	1.33	1.33	1.34	1.35
440	1.28	1.33	1.31	1.31	1.29	1.29	1.30	1.30	1.30	1.31
531	1.26	1.29	1.27	1.26	1.24	1.25	1.26	1.25	1.26	1.26

[a] S6 is SCOPW using Slater exchange approximation and six-points averages over the Brillouin zone.
[b] S is SCOPW using Slater exchange approximation.
[c] KS is SCOPW using Kohn and Sham exchange approximation.
[d] L is SCOPW using Liberman exchange approximation.
[e] S-RHF is Sl valence charge density + RHF core charge density.
[f] KS-RHF is KS valence charge density + RHF core charge density.
[g] L-RHF is Liberman valence charge density + RHF core charge density.

gonality functions when $\Psi_{\mathbf{k}_0}(\mathbf{r})$ is squared. The $\rho_{\mathrm{v-c}}$ term is around 10% of the plane-wave term ρ_{pw}. It is large only where the core charge density ρ_c is large, as it involves core wave functions. This $\rho_{\mathrm{v-c}}$ term is spherically symmetrized about each atom location for the self-consistent runs and for the form-factor calculations. The Fourier transform of the spherically symmetric terms is then taken in the well-known way:

$$\rho(k)=\int e^{i\mathbf{k}\cdot\mathbf{r}}\textstyle\sum_a\left[\rho_{\mathrm{v-c}}(\mathbf{r}-\mathbf{R}_a)+\rho_c(\mathbf{r}-\mathbf{R}_a)\right]d\mathbf{r}$$

$$=4\textstyle\sum_a e^{i\mathbf{k}\cdot\mathbf{R}_a}\displaystyle\int\left[\rho_{\mathrm{v-c}}(\mathbf{r})+\rho_c(\mathbf{r})\right]\frac{\sin kr}{kr}4\pi r^2dr\,,$$

where the sum is now over the two atoms in the basic cell at (0,0,0), and $(\frac{1}{4}a,\frac{1}{4}a,\frac{1}{4}a)$, and where four basic cells make up the usual crystallographic cell. The ρ_{pw} term is already defined by its Fourier components, and the absolute square then involves merely a sorting out of exponents.

IV. RESULTS

Tables VI–IX compare the experimental structure factors, corrected for thermal vibration and anomalous dispersion, with the results of several different SCOPW calculations for C, Ge, Si, and ZnSe, respectively. The theoretical procedures differ by the method used to approximate the exchange potential. The columns headed RHF are obtained by the superposition of relativistic Hartree-Fock free atoms. Those headed S contain results obtained using a Slater $\rho^{1/3}$ approximation, while KS and L indicate the use of Kohn-Sham and Liberman exchange, respectively. The symbol RHF added to any of these headings means that RHF cores have been substituted for those obtained in the calculation.

The main interest in the SCOPW results centers on the valence contribution to the form factors. For the 111 reflection, the valence contribution is around 47% for C, 12% for Si, and 6% for ZnSe and Ge. RHF form factors agree very closely with experiment for free atoms (gases). And in our experience, SCOPW core form factors vary little from free-atomic core form factors. This is the reason for the inclusions giving RHF core contributions together with SCOPW valence contributions to the form factors. Because of the accuracy of the RHF form factors for gases, it is felt that most of the remaining deviations of the SCOPW-RHF results from experiment can be attributed to the valence contribution.

TABLE VII. Comparison of experimental and calculated structure factors for Ge. Structure-factor units are electrons per crystallographic unit cell.

hkl	Expt	RHF	S	KS	L	S-RHF	KS-RHF	L-RHF
111	27.5±0.12	27.38	27.81	27.54	27.56	27.73	27.59	27.57
220		23.79	23.94	23.63	23.69	23.78	23.73	23.73
311		22.36	22.37	22.07	22.15	22.18	22.19	22.21
222		0.00	0.27	0.24	0.23	0.27	0.24	0.23
400		20.45	20.59	20.27	20.35	20.36	20.39	20.41
331		19.49	19.83	19.47	19.52	19.59	19.60	19.59
422		18.08	18.36	18.00	18.04	18.11	18.13	18.12
511		17.34	17.60	17.24	17.27	17.35	17.37	17.36
333		17.34	17.57	17.21	17.24	17.44	17.34	17.32
440		16.23	16.53	16.16	16.17	16.27	16.28	16.26
531		15.63	15.91	15.55	15.55	15.65	15.65	15.65

TABLE VIII. Comparison of experimental and calculated structure factors for Si. Structure-factor units are electrons per crystallographic unit cell.

hkl	Expt	RHF	S	KS	L	S-RHF	KS-RHF	L-RHF
111	11.12±0.04	10.53	10.88	10.70	10.64	10.86	10.72	10.65
220	8.78±0.09	8.71	8.76	8.63	8.60	8.72	8.67	8.62
311	8.05±0.07	8.16	8.09	7.99	7.98	8.03	8.04	8.00
222	0.22±0.04	0.00	0.22	0.19	0.23	0.22	0.19	0.23
400	7.40±0.14	7.51	7.53	7.42	7.45	7.45	7.48	7.47
313	7.32±0.12	7.18	7.35	7.22	7.26	7.27	7.28	7.29
422	6.72±0.06	6.70	6.81	6.67	6.71	6.72	6.74	6.74
333	6.43±0.08	6.44	6.50	6.37	6.39	6.40	6.43	6.43
511	6.40±0.08	6.44	6.54	6.41	6.43	6.45	6.47	6.46
440	6.04±0.15	6.03	6.16	6.01	6.03	6.06	6.07	6.06
444	5.00±0.10	4.97	5.11	4.95	4.94	5.00	5.06	4.98

It can be seen that KS and L come very close to RHF for the high-order reflections where the valence contribution is almost negligible. In other words, these treatments of the exchange potential give a description of the core that is close to the true Hartree-Fock. One also sees that the experimental results depart from the free-atom RHF calculation for the 111 and 222 reflections in C; the 111 and 222 in Si; the 111 in Ge; and 111, 200, 222, and 422 in ZnSe. The departure, however, is in the opposite direction from that observed for metals, where the first Fourier components are lower than the RHF values, indicating a delocalization of the outer electrons. Here on the contrary they are higher, suggesting a localization of the valence electrons. As can be seen, most of the exchange-model results are in qualitative agreement with the data. Thus, the band calculation generally improves on the free-atom values.

Let us now consider the comparison between theory and experiment in greater detail. For the 111 reflection, it appears that the various exchange models are not as satisfactory for Si as for the other crystals. This is in contrast to the fact that, when Slater's approximation is used for the exchange, the eigenvalues for Si are much better than those of C. But the band values for all the crystals are closer to experiment than the RHF values.

The 222 reflection has its surprises also. Here both Si and C band calculations give results in excellent agreement with experiment and improved with respect to the RHF values. But this is not the case for ZnSe. There the RHF value is too small, and the band calculations using any of the exchange approximations give even smaller values. The same result is found for the 420 difference line of ZnSe. But this trend is not general for all the difference lines, because one finds an improvement for the 200 coefficient over the RHF value. However, the 200 values from the different exchange approximations are not large enough to agree with experiment.

The results of the present calculation for diamond are compared with the results of earlier calculations in Table X. To compare with other calculations that do not include the core contribution, we have assumed that the RHF calculation of the 1*s* state accurately gives the core contribution. The 1*s* value listed in the second column of Table X has been subtracted from the measured value to give the experimental valence contribution listed in the third column, with which the remaining columns are compared. This line of reasoning is consistent with the observation that large RHF Fourier coefficients, which are mostly due to core contributions, agree with experiment.

It can be seen that all the crystal calculations (fifth–ninth columns of Table X) result in a higher (111) form factor than the free atom (fourth column) RHF value, correctly showing the localization of the valence electrons. The results of the present ARL model and those of Goroff and Kleinman both seem to be equally good in matching experiment, and the results of Clark are nearly as good. It should be noted that neither Goroff and Kleinman (who used 130 to 140 plane waves) nor

TABLE IX. Comparison of experimental and calculated structure factors for ZnSe. Structure-factor units are electrons per crystallographic unit cell.

hkl	Expt	RHF	S	KS	L	S-RHF	KS-RHF	L-RHF
111	158.55±1.6	155.80	157.68	156.22	156.48	157.31	156.61	156.71
200	14.86±0.55	11.22	11.72	11.15	11.60	11.90	11.12	11.37
220	189.80±2.0	189.79	191.14	189.48	189.10	189.94	189.56	189.62
311	129.10±2.0	125.90	126.40	125.50	125.02	125.37	125.32	125.42
222	11.63±0.6	10.33	9.61	9.50	9.93	9.94	9.67	9.79
400	162.31±1.8	162.13	163.57	162.51	161.43	161.79	161.94	162.06
331	109.55±2.0	109.47	111.13	110.34	109.45	109.81	109.93	109.92
420	12.09±0.7	11.59	10.85	11.08	11.33	11.19	11.19	11.30
422	140.56±1.8	143.30	145.37	144.43	142.89	143.39	143.62	143.62
440	128.76±1.7	128.86	131.05	130.19	128.34	129.05	129.24	129.15
531	88.37±1.3	88.29	89.74	89.18	87.82	88.36	88.48	88.42

TABLE X. Experimental and calculated valence charge densities for diamond. The RHF 1*s*-state value given in the second column was subtracted from the experimental values of Table VI to get the experimental valence contribution of column 3. Structure-factor units are electrons per crystallographic unit cell.

hkl	RHF 1*s*	Expt	RHF	KP[a]	B[b]	C[c]	GK[d]	Aerospace Research Laboratory
111	1.92	1.40	1.11	1.24	1.29	1.39	1.43	1.38
220	1.79	0.19	0.17	0.01	0.12	0.15	0.22	0.15
311	1.72	−0.06	0.03	−0.20	−0.14	−0.03	−0.05	−0.07
222	0.00	−0.14	0.00	−0.15	−0.13	−0.06	−0.11	−0.12
400	1.62	−0.14	−0.03	−0.13	−0.11	−0.05	−0.11	−0.10
331	1.56	0.02	−0.04				0.04	−0.03
422	1.47	−0.05	−0.03				0.08	−0.06
333	1.42	0.00	−0.02				0.12	−0.08
511	1.42	0.00	−0.02				0.08	−0.06

[a] Reference 13.
[b] Reference 14.
[c] Reference 15.
[d] Reference 16.

ARL (using 220 to 230 plane waves) obtained convergence as to eigenvalues versus the number of plane waves. However, this seems to have little effect upon the 111 Fourier coefficient of the charge density. The other materials considered in this paper are well converged with respect to both charge density and energies.

V. CONCLUSIONS

In most cases the SCOPW calculations predict qualitatively the departure of the experimental results from the free-atom superposition model. The most clear-cut example is given by the change of the 222 structure factors for the group-IV elements from the RHF values to the SCOPW values. That is, the covalent bonds, pointing toward the corners of the tetrahedron, are formed in the charge densities of the SCOPW results. When charge differences (antisymmetric parts of the potential) are allowed, as in the zinc-blende ZnSe, this effect seems to be hidden. The correct trend (increase in magnitude) is also found in the 111 coefficients of all the crystals and the 200 of ZnSe.

On the other hand, the agreement with the experiments selected is not in general quantitative. In other words, this otherwise very successful model fails when it comes to evaluate a ground-state property. One is not necessarily surprised, since the quantity minimized is the energy, which is very insensitive to details of the wave function, while the charge density is strongly affected by them. Since the outstanding approximation here affects the exchange potential, it is natural to associate it with this difficulty, as was done earlier by Arlinghaus.[36] It follows that further improvements in the treatment of exchange and correlation can benefit from a comparison with accurate charge-density measurements. These should become increasingly available as further interaction with theory will show the need for them.

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[36] F. J. Arlinghaus, Phys. Rev. **153**, 743 (1967).