Calculation of the Compton profile of beryllium

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A calculation of the Compton profiles of beryllium is presented. The wave functions are obtained from an *ab initio* calculation with the use of the pseudopotential approach within the local-densityfunctional approximation. The calculated anisotropic profiles are in excellent agreement with experiments. The directional profiles are also in good agreement except for a small discrepancy which can be improved by the inclusion of the effects of correlation in an approximate way.

I. INTRODUCTION

Beryllium metal is a very attractive candidate for theoretical and experimental investigations because of its anomalous properties and its simple atomic and crystal structures. Beryllium has a hexagonal close-packed crystal structure with only two core electrons $(1s^2)$ and two valence electrons $(2s^2)$ per atom. One common way to investigate the momentum distribution of the electrons is to examine Compton profiles. Experimentally these profiles can be measured directly from the photon scattering pattern, and theoretically they can be calculated using wave functions obtained from band-structure calculations. A comparison between theoretical and experimental profiles then serves as a test of the accuracy of the calculated wave functions. Several experimental measurements of the Compton scattering profiles¹⁻⁶ have been carried out in recent years to determine the electron momentum distribution. Because of recent improvements in the experimental facilities, the experiments by Hansen et al.⁵ using 412-keV gamma rays and Loupias et al.⁶ using 10-keV x rays are considered to be very accurate. Directional profiles along several symmetry directions were measured with a momentum resolution of 0.41 and 0.15 a.u. for the above experiments, respectively. Compton profiles of beryllium have been computed previously using several different methods $^{7-11}$; the calculated anisotropic behavior agrees qualitatively with the experimental results, but there is still a discrepancy in the amplitude.^{5,6} Since the directional Compton profiles measure the electron momentum distribution integrated over a plane perpendicular to a specific direction, they are very sensitive to the accuracy of the wave functions.

We have performed an *ab initio* calculation of the structural properties of beryllium¹² using the pseudopotential technique¹³ and the local-density-functional formalism¹⁴ with the atomic number as the only input. The lattice constants and the c/a ratio were successfully predicted by calculating the total energy of the system in the momentum space representation.¹⁵ The calculated bulk modulus and Poisson's ratio were also found to be in reasonably good agreement with the experimental values.

In this paper, we will present a calculation of the Compton profiles using the wave functions obtained from the *ab initio* calculation of beryllium.¹² It will be shown in

the following sections that the calculated results are in good agreement with the two recent experiments, e.g., they are closer to experiment than any of the previous calculations. In particular, the agreement is excellent for the anisotropic profiles. A rough estimate of the contribution of electron correlation is added to explain the remaining small discrepancies in the directional profiles. A brief report of our results has been published previously.¹⁶ The rest of this paper is organized as follows: The theoretical method is described in Sec. II, results are presented and discussed in Sec. III, and conclusions are given in Sec. IV.

II. CALCULATIONAL PROCEDURE

In this calculation the core electrons are taken to be atomiclike, and the valence electrons are treated by the pseudopotential approach.¹² The pseudopotentials are angular momentum dependent and are generated for the beryllium atom.¹⁷ A plane-wave basis set is employed to solve the Schrödinger equation self-consistently in the local-density-functional scheme^{13,14} and the Hedin-Lundqvist formula¹⁸ is used for the correlation energy. The eigenfunctions, with the spin index ignored, can be written as

$$\Psi_{\vec{k},n}(\vec{r}) = \frac{1}{V} \sum_{\vec{G}} C_{\vec{k},n}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}, \qquad (1)$$

where V is the volume, n is the band index, and the summation is over the reciprocal-lattice vectors \vec{G} . The coefficients have to satisfy the normalization condition

$$\sum_{\vec{\mathbf{G}}} |C_{\vec{\mathbf{k}},\boldsymbol{n}}(\vec{\mathbf{G}})|^2 = 1.$$
(2)

The electron momentum distribution is obtained from the Fourier transform of the wave functions,

$$n(\vec{p}) = \sum_{n} \sum_{\vec{k}}^{BZ} \sum_{\vec{G}} \delta_{\vec{p},\vec{k}+\vec{G}} |C_{\vec{k},n}(\vec{G})|^2 \Theta(E_F - E_{\vec{k},n}), \qquad (3)$$

where E_F is the Fermi energy, $E_{\vec{k},n}$ is the energy eigenvalue of $\Psi_{\vec{k},n}(\vec{r})$, and BZ represents Brillouin zone.

The impulse approximation¹⁹ is often used to calculate the Compton profile; it is valid when the incoming photon



FIG. 1. (a) First Brillouin zone of the hexagonal-close-packed structure. The irreducible $\frac{1}{24}$ th portion of the fast Brillouin zone and the reciprocal-lattice vectors are drawn with symmetry points specified. (b) Special directions in the ΓMLA and ΓKHA planes.

has much larger energy than the electrons of the system and when the final energy of the scattered electron is much greater than the initial energy. With the assumption of the impulse approximation the Compton profile along a certain direction \hat{e} can be written as

$$J(q,\hat{e}) = \frac{1}{N} \sum_{\vec{p}} n(\vec{p}) \delta(\vec{p} \cdot \hat{e} - q) .$$
(4)

The Compton profile $J(q,\hat{e})$ is symmetrical with respect to q=0 because of time-reversal symmetry. It is also subject to the normalization condition

$$\int_{-\infty}^{\infty} J(q,\hat{e}) dq = 2 , \qquad (5)$$

which is equal to the number of valence electrons per unit cell divided by the twofold spin degeneracy. Substituting (3) into (4), the Compton profile is given by

$$J(q,\hat{e}) = \frac{1}{N} \sum_{n} \sum_{\vec{k}} \sum_{\vec{G}} |C_{\vec{k},n}(\vec{G})|^2 \Theta(E_F - E_{\vec{k},n})$$
$$\times \delta((\vec{k} + \vec{G}) \cdot \hat{e} - q) .$$
(6)

The summation over \vec{k} in (6) is changed into an integration using the tetrahedral method.²⁰ The 24 irreducible wedges of the Brillouin zone may contribute differently; hence a method of equivalent vectors¹⁰ is used to reduce the \vec{k} points to be in one irreducible wedge of the Brillouin zone only. A set of 196 \vec{k} points is chosen in one irreducible wedge of the Brillouin zone and 648 tetrahedra are generated to carry out the integral. If the number of \vec{k} points is increased from 196 to 288, the change in the profile along the $\langle 11.0 \rangle$ direction is of the order of 10^{-3} , with the largest change being 0.005. The isotropic profile is obtained by integrating (6) over all directions first, i.e., integrating over \hat{e} .

Four Miller-Bravais indices are often used for the hcp structure to specify directions in real space. For our purpose, the reciprocal-lattice vectors $\vec{G}_1, \vec{G}_2, \vec{G}_3$ are a more convenient set of basis vectors. A direction with respect to this basis is specified by three numbers in square brack-



FIG. 2. Comparison between the calculated valence Compton profile of the free beryllium atom (solid line) and that of the pseudoatom (- - -). The isotropic profile of the metal (- - -) and that of the free-electron gas (\cdots) are also shown.

ets: $[c_1c_2.c_3]$. A full set of equivalent directions is expressed by angular brackets: $\langle c_1c_2.c_3 \rangle$. Figure 1 shows the first Brillouin zone of the hcp structure and indicates several symmetry directions. The nearest-neighbor Be-Be direction is along $\vec{G}_1 + (c/a)^2 \vec{G}_3$ and can be expressed as $\langle 10.(c/a)^2 \rangle$ using this basis, where $(c/a)^2$ is equal to 2.46.

There are two major approximations in the current pseudopotential scheme: One is the frozen-core assumption²¹; the other is the smoothing of the valence wave functions in the core region.¹⁷ Since the oscillations of the valence wave functions in the core region are taken out, it is expected that this approximation will decrease the amplitude of the Compton profiles for large q and increase the values near q=0. An estimate of this difference is given by examining the beryllium atom. The Compton profile calculated from the atomic 2s pseudo-wavefunction as well as that from the real all-electron wave function are shown in Fig. 2. The long tail disappears in the pseudoatom profile and a higher central peak is obtained. However, the average difference between these two profiles is minor and is no greater than 1% of J(q=0). The difference of the core profiles between free beryllium atoms and solids is expected to be small. The effect arising from the core expansion in beryllium metal is less than 1%.²² Taking the frozen-core approximation, one can obtain the total profile for the beryllium crystal by adding the atomic 1s Compton profile to the crystal valence profile.

III. RESULTS AND DISCUSSION

For the free-electron gas, the Compton profile is a parabola with a cutoff at the Fermi momentum P_F . In the crystal the Bloch functions, with wave vectors $\vec{k} + \vec{G}$, deform the parabola and give rise to a tail for q larger than

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9	(00.1)	(10.0)	(11.0)	〈 10.1 〉	(11.1)	$\langle 10.(c/a)^2 \rangle$
0.0	1.4154	1.4048	1.3375	1.4062	1.4270	1.3723
0.1	1.4346	1.3768	1.3353	1.3968	1.4025	1.3669
0.2	1.3439	1.3260	1.3279	1.3536	1.3497	1.3498
0.3	1.2427	1.2579	1.3031	1.2883	1.2624	1.3015
0.4	1.1303	1.1724	1.2353	1.1727	1.1586	1.2133
0.5	1.0250	1.0713	1.1156	1.0415	1.0463	1.0855
0.6	0.9109	0.9461	0.9172	0.9089	0.9265	0.9250
0.7	0.7971	0.7927	0.7320	0.7500	0.7745	0.7316
0.8	0.6593	0.5970	0.5564	0.5903	0.5889	0.5375
0.9	0.4107	0.3784	0.3830	0.3989	0.3831	0.3619
1.0	0.1455	0.1771	0.2337	0.1836	0.1864	0.2132
1.1	0.0540	0.0745	0.0723	0.0707	0.0729	0.0881
1.2	0.0300	0.0330	0.0330	0.0331	0.0335	0.0386
1.3	0.0190	0.0179	0.0191	0.0206	0.0201	0.0220
1.4	0.0132	0.0118	0.0118	0.0157	0.0141	0.0144
1.5	0.0101	0.0091	0.0077	0.0130	0.0107	0.0105
1.6	0.0080	0.0082	0.0051	0.0111	0.0089	0.0078
1.7	0.0065	0.0090	0.0036	0.0091	0.0083	0.0064
1.8	0.0061	0.0083	0.0030	0.0075	0.0079	0.0057
1.9	0.0065	0.0071	0.0040	0.0061	0.0069	0.0053
2.0	0.0059	0.0057	0.0061	0.0051	0.0058	0.0051
2.5	0.0021	0.0023	0.0026	0.0020	0.0022	0.0025
3.0	0.0002	0.0002	0.0000	0.0002	0.0002	0.0001

TABLE I. Calculated valence Compton profiles along six directions. The momentum q is in a.u.

 P_F , as is shown in Fig. 2. For beryllium metal, the sharp edge at the Fermi momentum (1.03 a.u.) is rounded.

The calculated valence Compton profiles along several directions are listed in Table I. To compare with the experimental results, the calculated profiles are convoluted with the experimental resolution functions. Figure 3 shows the total directional profile along the (00.1) direction compared with the latest experimental results by Loupias $et al.^6$ The overall agreement is very good. Similar agreement is also found when comparison is made with the γ -ray measurements of Hansen *et al.*⁵ However, it is



0.10 0.05 J.... - J.1.0 0.00 - 0.05 0.0 0.5 1.0 q (a.u.) FIG. 4. Comparison between the calculations and the mea-

FIG. 3. Comparison of the calculated directional profile (solid line) with the experiment by Loupias et al. (Ref. 6) (circles). The theoretical curve is convoluted with the experimental resolution function.

sured anisotropies by Hansen et al. (Ref. 5) (crosses) for (a) $J_{00,1} - J_{10,0}$ and (b) $J_{00,1} - J_{11,0}$. Convoluted theoretical results are as follows: present calculation (solid line), linear combination of atomic orbitals (LCAO) (Ref. 7) (dotted line), and pseudopotential calculation by Rennert (Ref. 10) (dashed line). The LCAO result is taken from Ref. 5.



more appropriate to make detailed comparisons with the

anisotropic profiles, since the systematic deviations in-

herent in both theory and experiment can be removed

when one directional profile is subtracted from another.



FIG. 5. Comparison between the calculations and the measured anisotropies by Loupias *et al.* (Ref. 6) (crosses) for (a) $J_{00,1}-J_{10,0}$ and (b) $J_{00,1}-J_{11,0}$. Convoluted theoretical results are as follows: present calculation (solid line), LCAO (Ref. 7) (dotted line), and pseudopotential calculation by Rennert (Ref. 10) (dashed line). The last two sets of data are taken from Ref. 6.

Moreover, the small amplitude of anisotropic profiles (less than 5% of the peak of the total profile) demands very high accuracy in both theory and experiment. Figure 4 shows the comparison of the experimental anisotropies observed by Hansen et al.⁵ (γ -ray) with several theoretical calculations. The solid line is the present calculation. The $J_{00.1} - J_{10.0}$ profile is shown in Fig. 4(a), and $J_{00.1} - J_{11.0}$ in Fig. 4(b). Similar comparison with the experiment by Loupias et $al.^{6}$ (x ray) are shown in Figs. 5(a) and 5(b). It can be seen that the present results are in excellent agreement with both experiments, better than any previous calculations. The oscillatory behavior agrees not only qualitatively, but also quantitatively, including the amplitude, the peaks, and the zeros. This indicates that the present theoretical method is capable of reproducing the fine details of the electron momentum distribution.

It has been pointed out previously² that the general feature of the anisotropic profiles arises from the special shape of the second Brillouin zone. If the plane-wave states are used to fill the first two Brillouin zones,⁵ the anisotropies therein are similar to those observed in the oscillation behavior and positions of maxima, minima, and zeros. In a real beryllium crystal, the second band is partially filled and some electrons exist in the third band. Therefore, the magnitude of the anisotropies gives a crucial test of the correctness of the shape of the Fermi surface as well as the electron momentum distribution.

Despite the overall agreement, there is still a small discrepancy between theory and experiment when the directional profiles are compared on a finer scale. Figures



FIG. 6. (a) Differences between the calculated (this work) and experimental [Hansen *et al.* (Ref. 5)] Compton profiles for the $\langle 00.1 \rangle$, $\langle 10.0 \rangle$, and $\langle 11.0 \rangle$ directions. (b) Differences after the correlation correction is added.

6(a) and 7(a) show the difference between experiment and the present calculation for several directions. These differences are too small to be seen in Fig. 3. The overall magnitude of the discrepancies seems to be independent of direction, hence only an isotropic correction is needed. The difference, which is especially large for q near the Fermi momentum P_F of the free-electron gas (1.03 a.u. for



FIG. 7. (a) Differences between calculated (this work) and experimental [Loupias *et al.* (Ref. 6)] Compton profiles for the $\langle 00.1 \rangle$, $\langle 10.0 \rangle$, and $\langle 11.0 \rangle$ directions. (b) Differences after the correlation correction is added.

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Be), suggests that the correction from correlation effects may be important. This contribution can be estimated by considering the momentum distribution for a correlated homogeneous electron gas as proposed by Rennert¹⁰:

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$$n(p) = \begin{cases} 1 - a \left[\frac{p}{p_F} \right]^2 & \text{for } \frac{p}{p_F} < 1 \\ \frac{a}{(b-1)^2} \left[b - \frac{p}{p_F} \right]^2 & \text{for } 1 < \frac{p}{p_F} < b \end{cases}$$
(7)

The value of a was taken to be 0.16 which is consistent with the random-phase-approximation (RPA) calculation by Daniel and Vosko²³ and b=1.476 as required by normalization. This correction is added to the calculated profiles of beryllium as an estimate of the effects of electron correlation. Figures 6(b) and 7(b) show the final differences between the theory and the two experiments. A significant improvement is found, and the discrepancies are reduced almost by a factor of 2. This comparison indicates that even a rough estimate of correlation contributions can explain the main part of the discrepancies obtained previously. However, more advanced theories of electron correlation appropriate for anisotropic inhomogeneous systems are needed in order to obtain further corrections. The remaining differences between theory and experiment are consistent with what we would expect in this theoretical approach. With the use of the pseudopotential scheme, oscillations near the core region are taken out, and therefore the profiles are underestimated for large q and overestimated for small q.

IV. CONCLUSION

In summary, the calculated and observed Compton profiles of beryllium are in excellent agreement. Even without the addition of a small correlation contribution the results are very good. This agreement indicates that the local-density-functional scheme together with the pseudopotential approach can give accurate wave functions describing the behavior of valence electrons in the solids. Having accurate directional profiles, it would be interesting for future studies to examine the relation between the momentum distribution in \vec{k} space and bonding in real space.

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