High-Resolution Compton Scattering Study of Li: Asphericity of the Fermi Surface and Electron Correlation Effects

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We present high-resolution Compton scattering spectra from Li single crystals together with corresponding highly accurate local-density-approximation (LDA) based computations. The data are analyzed to obtain Fermi surface radii along the three principal symmetry directions; the maximum measured anisotropy is found to be (4.6 ± 1.0)%. Comparisons between the measured and computed spectra clearly reveal departures from the conventional one-particle LDA picture of the ground state momentum density of the electron gas. This study establishes the potential of Compton scattering as a tool for investigating Fermiology-related issues in materials.

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It is well known that in a Compton scattering experiment one measures the momentum distribution [1]

$$J(p_z) = \int\int n(\mathbf{p})\, dp_x\, dp_y\,, \tag{1}$$

where $n(\mathbf{p})$ is the ground state electron momentum density,

$$n(\mathbf{p}) = \sum_i \left| \int \Psi_i(\mathbf{r}) \exp(i\mathbf{p}\cdot\mathbf{r})\, d\mathbf{r} \right|^2, \tag{2}$$

in terms of the electron wave functions $\Psi_i(\mathbf{r})$. The summation in (2) extends over all occupied states. Therefore, the Compton profile $J(p_z)$ contains fingerprints of Fermi surface (FS) breaks in the underlying 3D momentum distribution $n(\mathbf{p})$. The size of the FS discontinuity in the momentum density and its possible renormalization due to electron-electron correlations is a fundamental property of the ground state electronic structure, inaccessible to other $\mathbf{k}$-resolved spectroscopies such as angle-resolved photoemission, the de Haase–van Alphen effect (dHvA), and positron annihilation [2]. This unique capability of the Compton technique for exploring Fermiology-related issues has, however, been difficult to exploit to date because the momentum resolution available using γ-ray sources is not adequate for this purpose. The advent of high intensity, high energy, well polarized synchrotron sources removes this limitation and offers new opportunities for developing Compton scattering as a tool for investigating spectral properties of the electron gas at and near the Fermi energy in wide classes of materials [3].

With this motivation, we present in this Letter a high-resolution synchrotron-based Compton study of Li single crystals [4], and identify, for the first time, Fermi surface signatures in the data. The presence of a 2D integral in Eq. (1) implies that the structure associated with FS crossings will generally be more apparent in the derivatives of $J(p_z)$, rather than $J(p_z)$ itself. Accordingly, parallel highly accurate computations of the Compton profiles (CP's) within the band theory framework are reported; we are not aware of a previous calculation of CP's in the literature where the line shape in the derivative spectra has been properly computed. Comparisons between the measured and computed Compton spectra clearly reveal departures from the simple one-particle local-density-approximation (LDA) based picture of the momentum density.

It is noteworthy that the Compton experiment essentially measures a ground state property of the electron gas [5] in contrast with techniques such as dHvA and angle-resolved photoemission. Also, the Compton experiment, which involves a photon in–photon out situation, is neither surface sensitive like angle-resolved photoemission nor defect sensitive like dHvA or positron annihilation. Despite these advantages it is most sensible to view Compton as complementary to other $\mathbf{k}$-resolved spectroscopies, especially in investigating complex materials.

The measurements were carried out with a Compton scattering spectrometer installed at the AR-NE1 beam line of the National Laboratory for High Energy Physics [6]. Single crystals of Li grown by a modified Bridgman technique were used to obtain three disklike 4 mm thick samples with normals along the [100], [110], and [111] directions. The energy of the incident x rays was chosen to be 59.38 keV, with the scattering angle set at 160° [7]. The overall momentum resolution of the spectrometer is estimated to be 0.12 a.u. (FWHM)—about 8% of the Brillouin zone size; much of the earlier work with

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γ-ray line sources involves poorer resolutions, 0.37 a.u. or more. The Compton profiles were obtained from the raw energy profiles of the scattered x rays by generally following the data processing procedure described in Ref. [8]. The question of subtracting an appropriate background from the raw data was investigated extensively. In the final data presented here, instead of using the step at the K edge, the calculated core electron profile was used to determine the functional form of the background noise in the range of $-8 \leq p_z \leq -4$ a.u. and $+4 \leq p_z \leq +8$ a.u.; the results are insensitive to the specific choice of momentum range used in this fitting procedure. An independent experiment was carried out to confirm that the background contribution so estimated was mostly due to the inelastic scattering in the analyzer and is well represented by a linear function of the channel number of the imaging plate readout. The double Compton scattering events were simulated by a Monte Carlo method [9]; the total area under such events was found to be 3.6% of the single scattering events. In estimating error bars on the data, the complex relationship between the number of photons absorbed by the imaging plate, the uniformity of the imaging plate response, and the electronic noise generated in the readout process was taken into account following the work of Ref. [10]. Finally, the data were filtered to remove some short period fluctuations of small amplitude. The filtering process does not worsen the momentum resolution by more than a few percent.

Concerning computational details, our calculations use the all electron charge self-consistent Korringa-Kohn-Rostoker band structure scheme; the crystal potential is based on the von Barth–Hedin local density approximation to the exchange correlation functional, and possesses the muffin-tin form [11]. The band structure problem was solved to a high degree of self-consistency (energy bands, Fermi energy, and crystal potential converged to about 1 meV) for the bcc Li lattice ($a = 6.6163$ a.u.) before proceeding with Compton calculations [12]. Lam-Platzman corrections to the CP's were obtained using the occupation number density for the uniform electron gas [13]. For CP computations, the momentum density $n(p)$ in Eq. (1) was evaluated on a mesh with $87\,265 \times 177$ **p** points extending to about 5.0 a.u. This fine mesh, which corresponds to 87 265 *ab initio* **k** points in the irreducible 1/48th of the Brillouin zone, with each **k** point translated to obtain 177 **p** points using reciprocal lattice vectors, is necessary to properly treat Fermi surface breaks and the rather long range of the momentum density. In order to compute the 2D integral in Eq. (1) efficiently, vectorized versions of the linear tetrahedron method in which one zooms in on the momentum region in the vicinity of the Fermi surface breaks (with a concomitant increase in the effective density of **p** points) were developed. The CP's of Li presented here involve no essential approximation beyond the basic LDA, various other approximations such as the muffin-tin form of the potential are believed not to be significant. The final CP's were computed over a momentum mesh of 0.001 a.u. and are accurate to a few parts in 10^4.

We discuss our results with reference to Figs. 1–3. The overall shapes of the measured Compton profiles as well as their first and second derivatives are seen to be similar to the theoretical predictions. Focus first on the dashed curves in Fig. 2 which give the theoretical derivative spectra without resolution broadening. The structure originating from Fermi surface crossings is easiest to understand in terms of these curves. The most prominent "break" is seen to occur around 0.6 a.u., but the precise value differs along various directions indicating distortion of the free electron sphere. The crystal potential also induces images of the Fermi surface at higher momenta. These images, albeit weak, are centered at the fcc reciprocal lattice points $K_n \neq 0$, but get projected into the Compton spectra due to the 2D integral of the momentum density involved in Eq. (1). Along the [100] direction, the feature b_1 at about 0.4 a.u. is the projection of the $K = (1, 1, 0)$ centered Fermi surface image which is encountered before we reach the main break a_1 at 0.6 a.u. This is also the case of the [111] direction, however, the corresponding breaks b_3 and a_3 are closer together due to the particular geometry of the fcc reciprocal lattice; along the [110] direction, the break b_2 at around 0.75 a.u. turns out to lie beyond the break a_2.

When theoretical spectra are broadened to reflect experimental resolution, solid lines in Fig. 2, we see that, while FS breaks a_1-a_3 in the first zone continue to be distinct, this is less the case with b_1-b_3 arising from higher zones. A comparison with the corresponding experimental spectra clearly shows the presence of a_1-a_3. The data are also consistent with theoretical features

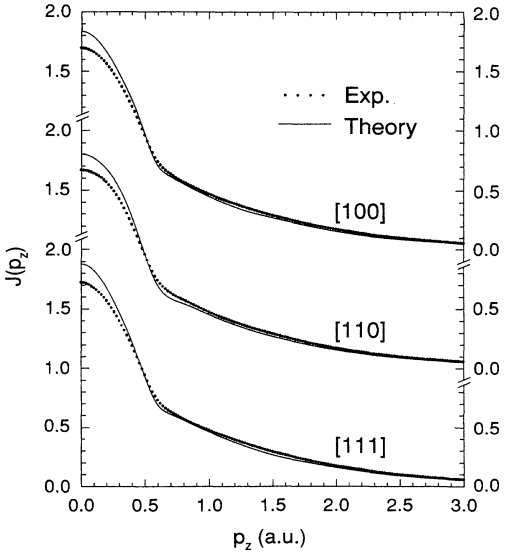

FIG. 1. Measured Compton profiles along the three principal symmetry directions are compared with the corresponding theoretical profiles broadened to reflect experimental resolution.

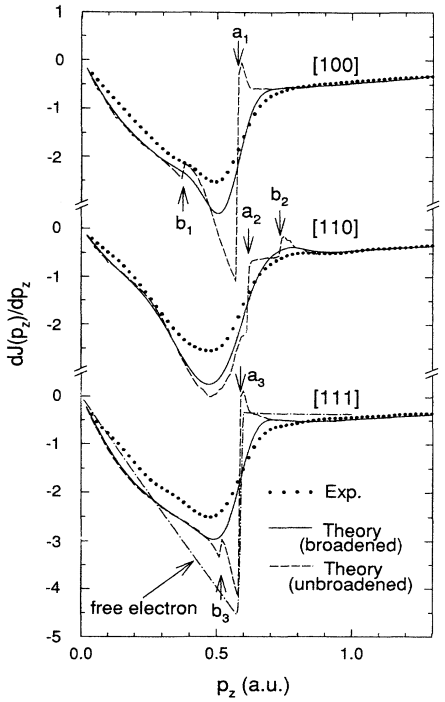

FIG. 2. Same as Fig. 1, except that this figure refers to the first derivative dJ/dp_z of the Compton profile. The theoretical curves without resolution broadening (dashed) are shown to highlight sharp structure related to Fermi surface crossings. The free electron prediction is shown on the [111] curve. a_1-a_3 and b_1-b_3 denote Fermi surface breaks discussed in the text. The error bars (not shown) are approximately of the size of the data points.

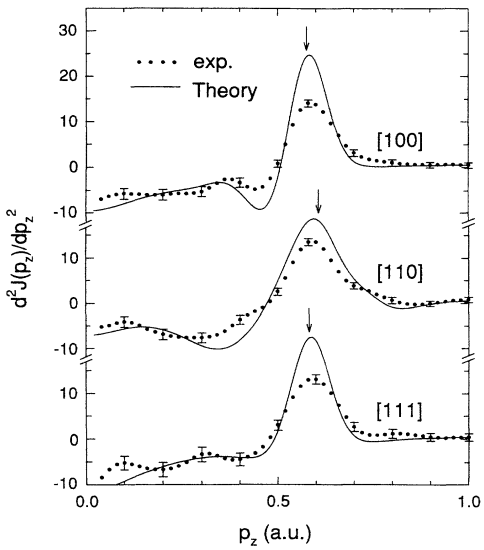

FIG. 3. Same as Fig. 1, except that this figure shows the second derivative d^2J/dp_z^2. Arrows denote the positions of the theoretical Fermi surface radii.

b_1-b_3, although a higher experimental resolution will be necessary to determine the positions of breaks b_1-b_3 accurately.

The values of the three principal Fermi surface radii can be obtained via the positions of the peaks in the second derivative spectra, Fig. 3. We emphasize, however, that the actual radii differ slightly from the peak positions in Fig. 3, since the FS breaks sit on an underlying distribution which is asymmetric. We have studied this effect extensively by considering model distributions chosen to mimic various aspects of the observed spectra (e.g., resolution broadening and size and width of the FS discontinuity). Our analysis indicates that the shift in the position of the second derivative peak in relation to the FS radius arises mainly from the presence of resolution broadening in the data, and that the size of this shift can be determined by comparing peak positions in the theoretical spectra with and without resolution broadening (the later shown by arrows in Fig. 3), since the overall shapes of the theoretical and experimental spectra in Figs. 1–3 are very similar.

The final experimental radii deduced from the data of Fig. 3 are (in a.u.) $k_{100} = 0.577 \pm 0.004$, $k_{110} = 0.604 \pm 0.004$, and $k_{111} = 0.586 \pm 0.004$. The corresponding theoretical values in the present band computation are (in a.u.) $k_{100} = 0.5764$, $k_{110} = 0.6112$, and $k_{111} = 0.5843$. The maximum deviation from sphericity in the FS of Li can be represented by the parameter $\delta = (k_{110} - k_{100})/k_0$, where $k_0 = 0.589$ a.u. is the free electron radius. This experiment yields $\delta = (4.6 \pm 1.0)\%$, compared to our theoretical value of 5.9%.

The FS of Li has been investigated very recently via the positron annihilation 2D correlation technique [14], obtaining $\delta = (4.7 \pm 0.2)\%$; an older positron study [15,16] gave a value of $(2.8 \pm 0.6)\%$. On the theoretical side, computations based on the LDA (such as the present one) yield values of δ lying between 5.5% and 6.0%; the inclusion of nonlocal corrections to the potential leads to a less anisotropic Fermi surface reducing δ values by roughly a factor of 2 [17]. Keeping these results in mind, our measured value of $\delta = (4.6 \pm 1.0)\%$ is consistent with the view that correlation effects beyond the LDA reduce the value of δ in Li but not as much as was implied by some earlier experiments [15] or computations [17].

Despite an overall similarity of shape between theory and experiment in Figs. 1–3, we see already from Fig. 1 that the measured Compton profiles are below the calculations for momenta within the FS with the situation reversing itself at higher momenta. In this connection, we made an extensive effort to analyze various corrections to the Compton data, some standard (such as multiple scattering), and others more specific to the present synchrotron data (e.g., inelastic scattering in the analyzer) but find our experimental results to be highly robust, leading us to conclude that the discrepancy in Fig. 1 represents effects of correlations on the momentum density of the electron gas beyond the local density approximation [18]. Figures 2 and 3 further show that the main FS breaks a_1-a_3 are sharper in the theory than the measurements consistent

with the expectation that correlations will reduce the size of the FS discontinuity compared to that implicit in our computations employing the independent particle picture.

In summary, we have presented high-resolution Compton spectra of Li single crystals together with corresponding highly accurate LDA based computations. The data allow the determination of Fermi radii via the Compton technique for the first time, on the one hand, and show unambiguous signature of deviations of the shape of the momentum density in the solid from the independent particle type band theory picture, on the other hand. This study establishes the potential of high-resolution Compton scattering as a tool for investigating Fermiology-related issues, and indicates its capabilities as a direct probe of hitherto inaccessible correlation effects such as the size of the momentum density discontinuities. The new low emittance, high energy light sources now coming on-line will yield improvements in resolution by factors of 3 to 6 depending on the type of spectrometer (i.e., ~0.02 a.u. FWHM, or, equivalently, on the order of 1% of the Brillouin zone diameter in Cu). The applicability of the Compton technique in investigating Fermiology and related electron correlations effects in wide classes of simple and complex systems can thus be anticipated.

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