Nonlocal Exchange-Correlation Effects in the Total Compton Profile of Copper Metal

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The ⟨110⟩ directional total Compton profile of copper metal has been measured by inelastic scattering of 412-keV γ radiation with special care for the multiple-scattering correction. The discrepancy between local density-functional band-structure calculations of the Compton profile and the experiment is attributed to a correction density functional, which clearly displays features due to nonlocal exchange-correlation effects.

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The Hohenberg-Kohn-Sham density-functional formalism[1] in the local-density approximation (LDA) to the exchange-correlation (XC) energy functional provides the theoretical basis of most modern first-principles calculations of the electronic structure of solids. Although some progress has been made,[2-5] a generally accepted explanation of the success of the LDA and a systematic improvement is still lacking, however. In order to judge the merits of methods beyond the LDA it is of prime importance to have accurate experimental data available which can be interpreted unambiguously within the conceptual framework of the ground-state density-functional theory. Such data can be provided by γ-ray scattering experiments[6] in the form of crystal structure factors,[7] i.e.,the Fourier coefficients of the ground-state charge density, or Compton profiles,[8,9] i.e., the projection of the ground-state momentum density on the scattering vector. Being the simplest transition metal, copper is an ideal testing ground for theoretical methods.[5] The charge-density structure factors[10] and the Compton-profile anisotropies[11] of copper have been measured previously at the Hahn-Meitner-Institut. Density-functional theory has been employed for the self-consistent calculation of charge and momentum densities of copper by MacDonald *et al.*[12] and Bagayoko *et al.*[13,14] The structure factors have been computed fully relativistically and without shape approximations for the potential by the linearized augmented-plane-wave (LAPW) method.[12] Structure factors[13] and Compton profiles[14] are available from full-potential band-structure calculations, where the wave functions are expanded within a large basis of linearly combined Gaussian orbitals, i.e., the LCGO method. Compton profiles of copper have also been computed by the modified augmented-plane-wave (MAPW) method for the Chodorow potential.[15] The significant discrepancy between experimental[11,16] and theoretical Compton-profile anisotropies of copper is also observed for most transition metals (see references quoted in Bauer and Schneider[17]). This discrepancy is most probably not due to the LDA potential or numerical problems in the band-structure calculations,[17] but to the local approximation for the momentum-density XC-correction functional[18,19] which has to be added to the results of the Kohn-Sham equations. This LDA correction is isotropic and does not affect the Compton-profile anisotropies, but significantly improves the agreement between theory and experiment for the total Compton profiles of beryllium.[20] Because of a large amount of multiple scattering, the error bar for the experimental total Compton profiles of copper in Ref. 11 turned out to be of the same magnitude as the XC-correction term. Therefore, we report here a more accurate experimental total Compton profile in the ⟨110⟩ direction, compare the results with density-functional band-structure calculations,[14] and discuss the observed discrepancies.

By the Compton spectrometer installed at the Hahn-Meitner-Institut[9] the energy-dependent cross section of 412-keV γ photons scattered through 165° is measured with a resolution of 0.41 a.u. of momentum at the Compton peak. Four rectangular single-crystal plates of 4×4-cm^2 cross section cut with faces parallel to (110) and thicknesses of 0.6, 1.0, 1.4, and 3.0 mm have been used for the measurements to get a feeling for the reliability of the multiple-scattering correction. To assure reproducibility and to increase statistical accuracy, a large number of photons have been collected in separate runs. Compton profiles are derived from the raw data by the conventional data processing,[8,21] assuming the validity of the impulse approximation[8] for the scattering process. The greatest experimental uncertainty is due to the multiple scattering of photons in the sample,[8] which has been corrected via

Monte Carlo computer simulation by a program[22] kindly provided by Prof. J. Felsteiner. The experimental error bar for the averaged profile in Fig. 1 is estimated from the scatter of the individually corrected measurements on different sample thicknesses. This error bar is a factor of 3 larger than counting statistics but affects only the slowly varying, general shape of the profile. Also included is a correction for the nonmonochromaticity of the primary γ radiation due to self-scattering in the source, which cannot be neglected for heavier elements.[23] The results are plotted in Fig. 1 as the difference between the LCGO density-functional calculation[14] and the experiment. The local XC-correction functional for the Compton profile is[18,19]

$$\Delta J^{\mathrm{LDA}}[\rho](q) = \int_{\text{unit cell}} \rho(\vec{r})\{j^h_{\rho(\vec{r})}(q) - j^f_{\rho(\vec{r})}(q)\}\, d^3r, \tag{1}$$

where $j^h_{\rho(\vec{r})}$ is the Compton profile of the homogeneous interacting electron gas of the (local) electronic charge density $\rho(\vec{r})$, normalized to one electron, and $j^f_{\rho(\vec{r})}$ is the same quantity for the homogeneous free-electron gas. The calculation of ΔJ^{LDA} is uncritical for solids.[17,20] The input for j^h is occupation numbers from Lundqvist[24] and the density-functional muffin-tin charge density as tabulated in Moruzzi, Williams, and Janak.[25] $-\Delta J^{\mathrm{LDA}}$ is plotted in Fig. 1 separately to indicate the significant improvement which is achieved. In contrast to the simple metal beryllium,[20] significant deviations are still observed, however. Figure 1 also shows that the semiempirical Chodorow potential to a certain extent successfully mimics the XC effect at low momentum transfer q.[15] The discrepancy at high momenta could point to a slightly too small high-momentum cutoff in the Compton profile integration routine employed in Ref. 15.

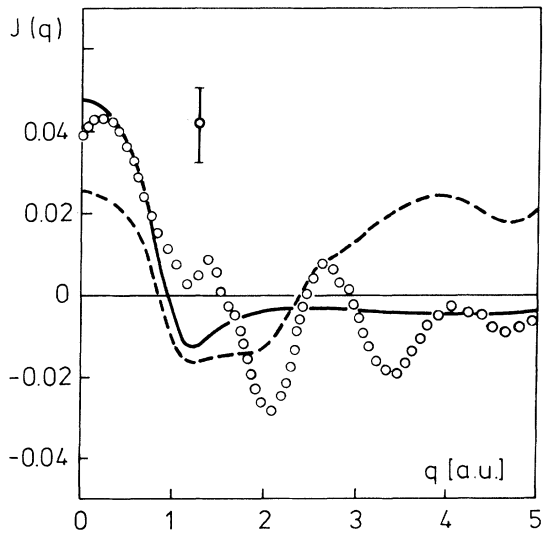

FIG. 1. Copper ⟨110⟩ Compton profiles. Circles: The difference between the Kohn-Sham local density-functional band-structure theory (Ref. 14) augmented by Hartree-Fock free-atomic-core Compton profiles (Ref. 32) and the experiment. Continuous curve: The XC-correction ΔJ^{LDA}, Eq. (1). Dashed curves: The difference between the Kohn-Sham local density-functional theory (Ref. 14) and the Chodorow potential band-structure theory (Ref. 15). The theoretical results are convoluted by a Gaussian with a full width at half maximum of 0.41 a.u. of momentum to account for the experimental resolution smearing (Ref. 9).

In Fig. 2 the difference between the complete density-functional theory, i.e., the correction term ΔJ^{LDA} included, and the corrected experiment for the copper ⟨110⟩ Compton profile is displayed. The similarity of Fig. 2 with the Compton-profile anisotropies which involve the ⟨110⟩ direction[11] is striking and a consequence of the Fermi-surface topology in the periodic zone scheme, as explained below. In principle the oscillations have been observed already in terms of the disagreement of experiment and theory in the Fourier-transformed Compton profile $B(\vec{r})$[26] at the first lattice translation.[11,17] Here we observe that it is essentially this one Fourier component which characterizes the failure of the local density-functional theory.

Since we found[17] that the band-structure results of Ref. 14 are sufficiently accurate, Fig. 2 can only be explained following the discussions of Schneider and co-workers.[11,27] The first approximation for the momentum density of copper is a free-electron Fermi sphere plus a spherically symmetric $3d^{10}$ atomic contribution. The hybridization introduces $3d$-electon holes into the occupied band states with Bloch vectors $\vec{k}$ outside the Fermi surface. The $3d$ holes significantly depopulate the otherwise essentially atomiclike momentum density in the interstitial region defined by the Fermi-surface volumes centered on reciprocal lattice vectors in the periodic zone scheme. The XY plane of reciprocal space is plotted in Fig. 2 in the appropriate scale. Indicated are the Brillouin-zone boundaries and the Fermi spheres of a face-centered cubic crystal with the lattice constant of copper. The Compton profile is the integrated momentum density in a plane normal to the scattering vector as a function of the momen-

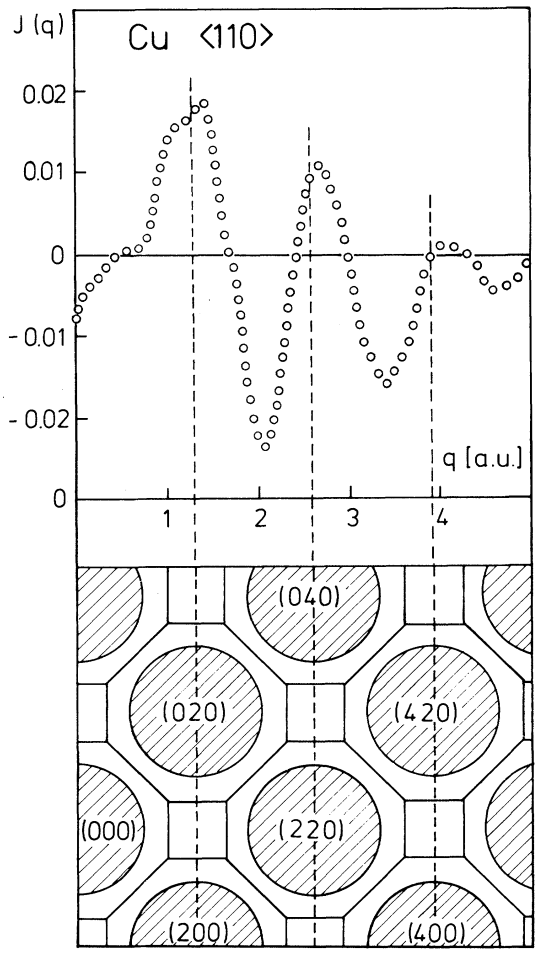

FIG. 2. Upper part: Difference between the local density-functional theory and the experiment (see text). Lower part: XY plane of the Brillouin zone and the Fermi surface of copper in the repeated zone scheme. The error bar of the experiment in Fig. 1 affects the general shape of the profile only. The oscillations shown here are much more significant.

tum transfer q. Some of the $\langle 110 \rangle$ Compton-profile integration planes are indicated in Fig. 2 by their intersection with the XY plane. It is clearly visible that the extrema of the difference between experiment and theory coincide with the extrema of the cross-sectional area of the intersected Fermi spheres. This is a strong indication that the Coulomb correlation transfers electrons from the "occupied" Fermi spheres into the "unoccupied" interstitial regions of reciprocal space, i.e., theory shows too much momentum density inside and too little momentum density outside the Fermi surfaces.

Our findings agree with the general experience[2-5,17] that the main error of the LDA is not due to an insufficient knowledge of the properties of the homogeneous electron gas, which are used to parameterize XC potentials and also the correction term Eq. (1). The observed error must then be attributed to "nonlocal" XC effects, which are by definition outside the range of the LDA. Since local density-functional theory satisfies the virial theorem,[28] the integral of the difference Compton profile in Fig. 2 multiplied by q^2 equals the nonlocal XC energy. Unfortunately a quantitatively reliable estimate of this quantity cannot be given to date because of the rather substantial experimental error of the base line (cf. Fig. 1). But it is obvious from Fig. 2 that the oscillations must render the integral very small. We believe that this is the first direct experimental evidence that the success of the local density-functional theory for the calculation of total energies and charge densities is largely due to a cancellation of sizable nonlocal XC contributions.

The effect cannot be explained by a procedure which works for the alkali metals,[29] i.e., by populating Bloch waves according to the occupation numbers of the interacting homogeneous electron gas. Instead, we interpret the difficulties as a combination of the renormalization of the quasiparticle and high-momentum components of resonances at higher binding energy, which might be too broad to be resolved by, e.g., photoemission experiments, but which become significant for the momentum density by energy integration. Whether these satellites are predominantly due to a coupling of the hole to collective oscillations as observed in silver[30] or are indicative of remnants of the atomic multiplet[31] cannot be decided from the copper data alone. In a search for clues, measurements of Compton profiles of nickel and silver will be undertaken in the near future.

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