Inelastic X-Ray Scattering as a Probe of the Many-Body Local-Field Factor in Metals

B. C. Larson,[1] J. Z. Tischler,[1] E. D. Isaacs,[2] P. Zschack,[3] A. Fleszar,[4] and A. G. Eguiluz[1,5]

[1]*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6030*

[2]*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

[3]*Oak Ridge Associated Universities, Oak Ridge, Tennessee 37831*

[4]*Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

[5]*Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200*

(Received 19 December 1995)

We report the first measurement of the many-body local-field factor $G(\vec{q},\omega)$ for a simple metal (Al) at large wave vectors. Inelastic x-ray measurements of the dynamical structure factor are analyzed using *ab initio* calculations of the noninteracting polarizability. Our measured $G(\vec{q},\omega)$ is in agreement with available theory for $q < 1.5k_F$, unlike earlier electron energy-loss results; however, for $q \sim 2k_F$ our $G(\vec{q},\omega)$ is a factor of 2 stronger than most theoretical predictions. We have also measured the polarizability for *noninteracting* electrons at a wave vector for which $G(\vec{q},\omega) \cong 1$. [S0031-9007(96)00863-0]

PACS numbers: 71.45.Gm, 78.70.Ck

Electron-electron interactions play a central role in determining many of the physical properties of metals, including the excitation spectrum. Consideration of these interactions in terms of the random phase approximation (RPA) by Bohm and Pines [1], and the introduction of exchange-correlation corrections by Hubbard [2], dating back more than forty years, have formed the basis of an enormous theoretical effort aimed at understanding the effects of electron-electron interactions at metallic densities.

In the case of the nearly-free-electron metals, the impact of the ion-core lattice (band structure) on the electronic excitations has been presumed to be small. However, recent x-ray measurements [3] and first-principles evaluations of the dynamical density response of Al [4,5] and Be [5] have shown that band structure effects cannot be neglected. Unfortunately, calculations of the effects of dynamical correlations for electrons propagating in the actual band structure of Al—or any other metal—are not yet available. It is then of interest that Fleszar, Quong, and Eguiluz [4] have suggested that x-ray *measurements* of the dynamical structure factor for large wave vectors could now be used to probe the details of the correlations in terms of a Hubbard-like many-body local-field factor (LFF) $G(\vec{q},\omega)$ [6].

In this Letter we report the first measurement of the many-body LFF for aluminum at large wave vectors. Our results were obtained from inelastic x-ray scattering measurements, combined with calculations of the dynamical density response for *noninteracting* electron-hole pairs. We find the experimentally determined LFF to be more than twice as strong as theoretical predictions [7–13] for the interacting electron gas in the critical $2k_F$ region. On the other hand, and contrary to electron energy-loss determinations [14], our measured LFF is in agreement with theory [7–13] for $q \leq 1.5k_F$. Our results indicate that the frequency dependence of the LFF is weak in the most interesting spectral region, in which the response contains the well-known double-peak structure of Al [15].

Furthermore, we have made the first identification of a wave vector transfer for which the "experimental" $G(\vec{q},\omega) \cong 1$ over a wide ω interval. This finding allows unique insight into the dynamics of electrons in a metal, since for this special wave vector the x-ray photons probe the response of "bare," or noninteracting, electron-hole pairs. Interestingly, we find that, *for this selective experimental condition*, the noninteracting polarizability calculated from Kohn-Sham [16] states is in excellent agreement with the loss spectrum up to $\hbar\omega \sim 35$ eV, and that it provides a fair approximation for even larger energies.

X-ray measurements of the dynamical structure factor $S(\vec{q},\omega)$ [17] were obtained on single-crystal aluminum samples using the Oak Ridge National Laboratory X-14 bend-magnet beam line at the National Synchrotron Light Source. The measurements were made in reflection geometry with 5.7 keV x rays for a range of wave vectors around $2k_F$ in the [013] and [001] directions (k_F is the Fermi wave vector; for Al, $k_F = 1.75$ Å^{-1}). Spectra were collected over an energy-loss range of ~80 eV with respect to the elastic line, using a sagittal-focusing, pyrolitic graphite analyzer crystal (~0.4° mosaic), in conjunction with a linear, position-sensitive detector. Nonuniformities [(±10–15)%] in the response of the mosaic analyzer-detector system were calibrated (using the elastic scattering) by scanning the energy of the incident beam over the energy range of the detector [Fig. 1(a)]. In order to ensure adequate statistical precision for the energy-loss measurements, we used a rather coarse 2.9 eV energy resolution (full width at half maximum of the elastic line). The tail of the elastic line [shown in Fig. 1(a)] was obtained assuming symmetry with the energy-gain

 0031-9007/96/77(7)/1346(4)$10.00

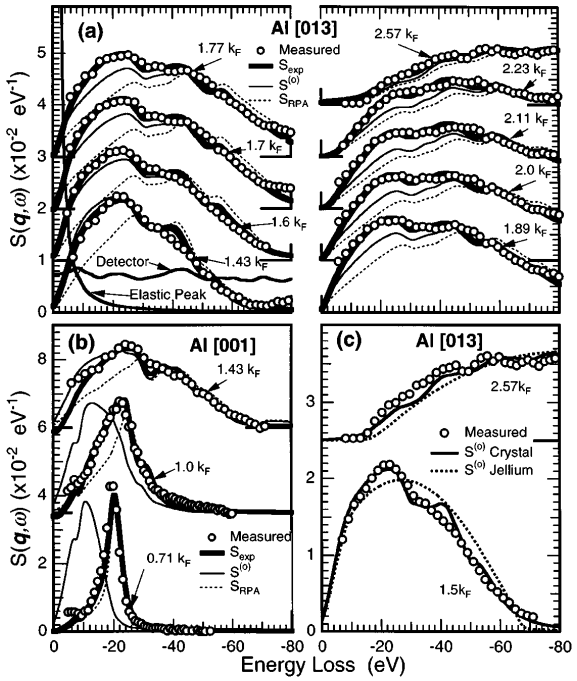

FIG. 1. (a),(b) Empty circles: measured $S(\vec{q},\omega)$ for Al along the [013] and [001] directions; thick solid line: $S_{\rm exp}$ corresponding to Eq. (1) for $G(\vec{q},\omega) = G_{\rm exp}(\vec{q},\omega)$ of Fig. 2; thin solid lines: loss spectra for noninteracting electrons, $S^{(0)}(\vec{q},\omega)$ [Eq. (1) for $\nu = 0$]; dotted lines: RPA spectra, $S_{\rm RPA}(\vec{q},\omega)$ [Eq. (1) for $G(\vec{q},\omega) = 0$]. (c) X-ray spectra for $q = q_0 = 1.5k_F$ [interpolated between $1.43k_F$ and $1.6k_F$ to correspond to $G_{\rm exp}(\vec{q},\omega) \cong 1$], and for $q = 2.57k_F$ [for which $\nu(q) \to 0$; solid lines: theoretical spectra for *noninteracting* electron-hole pairs (see text). (Calculations convoluted with the 2.9 eV measurement resolution.)

side of the elastic peak, and using measurements in the loss-free region ($\Delta E < 13$ eV) on the energy-loss side for $q = 2.57k_F$; this composite peak shape was scaled to the measured elastic peak at each wave vector and subtracted.

The open circles in Fig. 1 show $S(\vec{q},\omega)$ measured along the [013] and [001] directions. The absolute scale for $S(\vec{q},\omega)$ was determined by using the f-sum rule [17] and the measured data for $q \sim 1.7k_F$ [18]. The results of Fig. 1 show the well-known evolution of the excitation spectrum of simple metals, changing from a sharp plasmon loss for a relatively small wave vector ($q = 0.71k_F$) to the double-peak structure [15], which first appears for $q \sim 1.4k_F$. Note that a vestige of this structure remains even for the largest q in Fig. 1(a). These results are similar to those reported by Platzman *et al.* [19] and Schülke *et al.* [20]; however, the present data were obtained more closely spaced about $2k_f$ in order to investigate the q dependence of the many-body effect.

We discuss the physics contained in our data on the basis of the following expression for the dynamical structure factor:

$$S(\vec{q},\omega) = -2\hbar\Omega_N \mathrm{Im}\{\chi^{(0)}[1 - \nu(1 - G(\vec{q},\omega))\chi^{(0)}]^{-1}\}_{\vec{G}=0,\vec{G}'=0}, \quad (1)$$

where ν is the bare Coulomb interaction, $\chi^{(0)}$ is the so-called irreducible polarizability for *noninteracting* electron-hole pairs, and Ω_N is the normalization volume. All quantities inside the braces in Eq. (1) are matrices in reciprocal ($\vec{G}$) space; the braces as a whole represent the $\vec{G} = 0$, $\vec{G}' = 0$ element of the spatial Fourier transform of the density-response function $\chi(\vec{x},\vec{x}';\omega)$ [1,21]. Short-range correlations are introduced in χ via the many-body LFF $G(\vec{q},\omega)$; these correlations *are probed by the short wavelengths afforded by x rays.*

We emphasize that Eq. (1) is formally exact, since it amounts to a definition of $G(\vec{q},\omega)$ [22]. The evaluation of this quantity for a realistic model of a metal is an outstanding problem in condensed matter physics that, so far, has lacked experimental input. In this Letter we extract $G(\vec{q},\omega)$ from the measured inelastic cross sections through the use of Eq. (1), in conjunction with *ab initio* evaluations of the noninteracting "bubble" $\chi^{(0)}$.

This task is simplified considerably by the fact that, through explicit calculation, we have determined that the crystal local fields (i.e., the off-diagonal elements of the matrix $\chi^{(0)}_{\vec{G},\vec{G}'}$) are negligible for Al. Thus, all quantities entering Eq. (1)—in particular, the LFF—can be treated as scalars. (We note that this is not a universal result for the "simple" metals; for example, in the case of Cs, the matrix nature of the noninteracting response $\chi^{(0)}_{\vec{G},\vec{G}'}$ plays a crucial role [23].)

Now, $G(\vec{q},\omega)$ is in general expected to be complex for nonzero frequencies, a reflection of the inherent damping of the one-electron excitations. Kramers-Krönig transform of the data to obtain the Re $\chi_{\rm exp}$ is not possible because the need to remove the elastic line from the inelastic scattering limits the reliability of data for small ω's, and, furthermore, for most q's of interest, the response of the valence electrons overlaps that of core states ($\hbar\omega \approx 72$ eV), which are not included in our pseudopotential-based calculations [21]. Therefore, in this study we extract a complex LFF—which we denote $G_{\rm exp}(\vec{q},\omega)$—by a least-squares determination of Re $G_{\rm exp}(\vec{q},\omega)$ and Im $G_{\rm exp}(\vec{q},\omega)$ such that Eq. (1) matches the measured data over the 10–70 eV energy loss range on the basis of a *single* (complex) value for each wave vector. The results of this analysis are presented in Fig. 2, and the corresponding spectra $S_{\rm exp}$ are plotted in Figs. 1(a) and 1(b). The fact that $G_{\rm exp}(\vec{q},\omega)$ yields *quantitative* agreement with the measured data over a large range of q's and ω's indicates directly that the frequency dependence of the LFF is weak for the region sensitive to the many-body effect, $\hbar\omega < 35$ eV; tests with 10 eV frequency windows confirmed this result [24].

It is apparent from Figs. 1(a) and 1(b) that the many-body LFF makes a substantial contribution to the

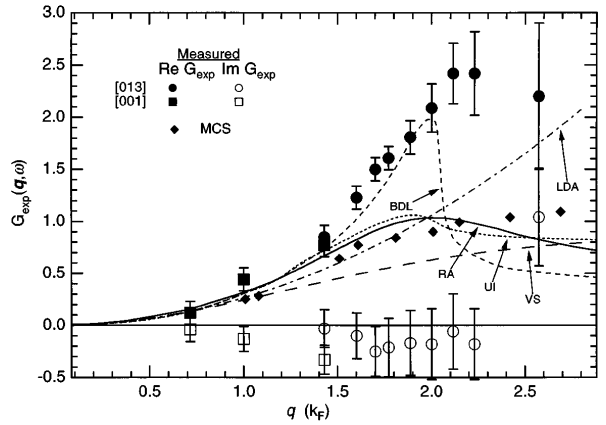

FIG. 2. Real and imaginary parts of the measured LFF, $G_{\rm exp}(\vec{q},\omega)$, for Al (full and empty symbols, respectively). Representative LFF's calculated for jellium with $r_S = 2.07$ are also shown; see text for details. The error bars for $G_{\rm exp}(\vec{q},\omega)$ correspond to a $\pm 5\%$ uncertainty in the measurements of Figs. 1(a) and 1(b).

measured intensities as soon as the wave vector transfers become large enough that the response is mainly incoherent, i.e., dominated by electron-hole pair excitation. In effect, the x-ray spectrum displays a clear "crossover" from a regime ($q \leq k_F$) for which the response is dominated by the average effects of the Coulomb interaction—i.e., the RPA, for which $G(\vec{q},\omega) = 0$, works reasonably well—to the regime ($q \geq k_F$) for which the many-body LFF plays a dominant role. Such a crossover is easily visualized in Figs. 1(a) and 1(b). *We emphasize that it is the large impact of the many-body effect for energies up to* $\hbar\omega \sim 40$ eV *that has allowed us to extract the LFF for Al.*

It is interesting to note that the effect of the LFF in the present problem is qualitatively similar to the continuum-exciton effect discussed at length by Hanke and Sham [25] in their seminal many-body calculations of the optical spectra of semiconductors. The exchange-correlation interactions built into the LFF—or the "electron-hole attraction" [25]—bring about a large enhancement of the low-ω side of the inelastic x-ray scattering spectrum of Al, in much the same way as the continuum-exciton effect in, e.g., Si. However, here the many-body effect takes place for large q's [26], while in the optical response it occurs for $q = 0$.

From Fig. 2 we have that, to a good approximation, the experimentally determined LFF is real. Thus, in the same figure we compare $G_{\rm exp}(\vec{q},\omega)$ with a sampling of the many real, *static*, LFF's reported for jellium with the density of Al, $r_S = 2.07$—namely, the results Vashishta and Singwi (VS) [8], Utsumi and Ichimaru (UI) [9], Richardson and Ashcroft (RA) [10], and Brosens, Devreese, and Lemmens (BDL) [11], as well as the local-density approximation (LDA) [16], and the quantum Monte Carlo simulations of Moroni, Ceperley, and Senatore (MCS) [12]. All the theoretical values (RA, UI, BDL, MCS) are in good agreement with $G_{\rm exp}(\vec{q},\omega)$ up to $q \sim 1.5k_F$. This result is consistent with the plasmon dispersion calculations for Al by Quong and Eguiluz [4] (which were performed in LDA, and agreed very well with electron energy-loss measurements), and resolves a long-standing difference between electron energy-loss measurements of the LFF [14] and theory [7–13]. However, in the important $q \rightarrow 2k_F$ incoherent-response regime, which has not been measured previously, the experimental LFF differs significantly—*it becomes much larger*—than the theoretical predictions.

This experimental finding, which clearly suggests that even in a simple metal such as Al the dynamical electronic correlations are quite strong, poses a challenge to theory. Although the result of BDL [11] agrees remarkably well with $G_{\rm exp}(\vec{q},\omega)$ up to $q \sim 2k_F$—*but not beyond*—the significance of this agreement is not at all obvious, since the calculations of BDL did not account for the screening of the exchange ladders. Furthermore, a *dynamical* LFF obtained by the same group [13] differs markedly from our measurement—for example, in the 20–30 eV range, its real part is closer to the result of MCS.

Referring to Fig. 2, we have that $G_{\rm exp}(\vec{q},\omega) = 1$ for $q \equiv q_0 \sim 1.5k_F$. Most importantly, this equality holds (approximately) over a large frequency interval—we argued above that our results are consistent with a weak ω dependence of the LFF for energies below $\sim$35 eV. What is striking about this result is that it means that for $q = q_0$, the x rays in effect probe the response of noninteracting electron-hole pairs. *This result affords a unique opportunity to probe the details of the bare excited-state band structure in a solid.*

In Fig. 1(c) we compare the experimental spectrum for $q = q_0$ with that calculated from Eq. (1) for $\nu(q) \equiv 0$ [or $G_{\rm exp}(\vec{q},\omega) = 1$], which we call $S^{(0)}(\vec{q},\omega)$. The agreement of the latter with experiment is extremely good, especially considering that the calculation contains no adjustable parameters, and that we are comparing absolute intensities. This agreement is possible only in the presence of a weak frequency dependence of $G(\vec{q},\omega)$.

One may ask whether such agreement is to be expected, since $S^{(0)}(\vec{q},\omega)$ is obtained from Kohn-Sham states [16], for which it is well known that there is no Koopmans-like theorem. Furthermore, the meaning of the wave vector q_0 is tied up with the fact that $G(\vec{q},\omega)$ was defined in Eq. (1) to include *all* the many-body correlations [22]—while the band-structure calculations underlying our extraction of $G_{\rm exp}(\vec{q},\omega)$ include exchange and correlation within the LDA [16]. However, we have also computed a fully "undressed" $S^{(0)}$ from eigensolutions of the ground-state problem in the Hartree approximation. The "true noninteracting" spectrum so obtained was indistinguishable [on the scale of Fig. 1(c)] with the $S^{(0)}$ we present in Fig. 1(c), obtained from LDA eignesolutions. Thus, at least within the context of this LDA-based test, the measured $G_{\rm exp}$ does contain the entire many-body effect, and

the response of (undressed) Kohn-Sham electrons is indeed the one being probed by the x rays for $q = q_0$.

As the Coulomb interaction and $\chi^{(0)}$ fall off for large q, electron-electron interactions become negligible. This large-q behavior of the spectrum ($q = 2.57k_F$) is also included in Fig. 1(c). As was the case for $q = q_0$, the noninteracting response calculated from eigensolutions of the density-functional ground state (in LDA) accounts rather well for the main features of the observed spectrum.

We note that the spectra for noninteracting electrons in jellium do not reproduce the data shown in Fig. 1(c) (this conclusion holds for all wave vectors). Thus, if $G_{\text{exp}}(\vec{q}, \omega)$ were to be obtained on the basis of $\chi^{(0)}$ for jellium (Lindhard function), a substantial ω dependence would be required—unlike our experimental result for Bloch electrons. (In fact, that is what was done in the past to extract static LFF's from electron [14] and x-ray scattering [26] data; in light of the spurious strong ω dependence just alluded to, such results are ambiguous.)

In summary, we have presented the first measurement of the dynamical many-body LFF for Al in the crucial $q \rightarrow 2k_F$ regime. Available theory [7–13] is in agreement with our LFF for $q < 1.5k_F$; the long-standing differences between theory and electron-energy loss data for these wave vectors can be attributed to an analysis of the data [14] based on the polarizability for electrons in jellium. On the other hand, our results indicate that many-body correlations are much stronger than predicted by theory for the larger wave vectors accessible to x rays. We hope these first experimental results for $q \geq 2k_F$ will stimulate fundamental theoretical work on the electron-correlation problem. The development of new capabilities at both second and third generation synchrotron facilities now opens the exciting prospect of performing similar experimental investigations for a large variety of systems, including transition metals.

Research sponsored by the U.S. Department of Energy under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. The measurements were performed using the NSLS. A. G. E. acknowledges support from National Science Foundation Grant No. DMR-9207747/9596022 and the National Energy Research Supercomputer Center.

[1] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).
[2] J. Hubbard, Proc. R. Soc. London A **243**, 336 (1957).
[3] W. Schülke *et al.*, Phys. Rev. B **33**, 6744 (1986); W. Schülke *et al.*, Phys. Rev. Lett. **59**, 1361 (1987).
[4] A. A. Quong and A. G. Equiluz, Phys. Rev. Lett. **70**, 3955 (1993); A. Fleszar, A. A. Quong, and A. G. Eguiluz, Phys. Rev. Lett. **74**, 590 (1995).
[5] N. E. Maddocks, R. W. Godby, and R. J. Needs, Europhys. Lett. **27**, 681 (1994); Phys. Rev. B **49**, 8502 (1994).
[6] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990), 2nd ed., p. 444.
[7] A. Holas *et al.*, Phys. Rev. B **20**, 4912 (1979); K. Awa *et al.*, Phys. Rev. B **25**, 3687 (1982); S. Rahman and G. Vignale, Phys. Rev. B **30**, 6951 (1984); J. E. Albarellos and F. Flores, J. Phys. F **15**, 1929 (1985); F. Green *et al.*, Phys. Rev. B **35**, 124 (1987); A. Gold and L. Calmels, Phys. Rev. B **48**, 11 622 (1993).
[8] P. Vashishta and K. S. Singwi, Phys. Rev. B **6**, 875 (1972).
[9] K. Utsumi and S. Ichimaru, Phys. Rev. B **22**, 5203 (1980); **23**, 3291 (1981).
[10] C. F. Richardson and N. W. Ashcroft, Phys. Rev. B **50**, 8170 (1984).
[11] F. Brosens, J. T. Devreese, and L. F. Lemmens, Phys. Rev. B **21**, 1363 (1980); F. Brosens and J. T. Devreese, Phys. Status Solidi B **147**, 173 (1988).
[12] S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995).
[13] J. T. Devreese, F. Brosens, and L. F. Lemmens, Phys. Rev. B **21**, 1349 (1980).
[14] P. Zacharias, J. Phys. F **5**, 645 (1975); P. C. Gibbons, S. E. Schnatterly, J. J. Ritsko, and J. R. Fields, Phys. Rev. B **13**, 2451 (1976).
[15] P. M. Platzman and P. Eisenberger, Phys. Rev. Lett. **33**, 152 (1974).
[16] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[17] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966), Vol. 1.
[18] The $\sim 0.4°$ mosaic spread of the ($\pm 2°$ acceptance) analyzer introduces a small ($\sim 0.1k_F$) departure from a truly constant wave vector over the ~ 80 eV range of the measurements. Thus, the q label for each measured spectrum shown in Fig. 1 refers to the q value at the elastic line. All calculations include this slight change in wave vector for a given ω scan; the f-sum rule was implemented after linearly interpolating between the data for $1.6k_F$ and $1.7k_F$.
[19] P. M. Platzman, E. D. Isaacs, H. Williams, P. Zschack, and G. E. Ice, Phys. Rev. B **46**, 12 943 (1992).
[20] W. Schülke, H. Schulte-Schrepping, and J. R. Schmitz, Phys. Rev. B **47**, 12 426 (1993).
[21] A. G. Eguiluz, A. Fleszar, and J. A. Gaspar, Nucl. Instrum. Methods Phys. Res., Sect. B **96**, 550 (1995).
[22] An equation of the form of Eq. (1) arises rigorously in time-dependent density functional theory; see M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996); A. G. Eguiluz (to be published).
[23] A. Fleszar, R. Stumpf, and A. G. Eguiluz (to be published).
[24] For $\hbar\omega \geq 40$ eV, the LFF determined using small "windows" oscillates about the value defined by $G_{\text{exp}}(\vec{q}, \omega)$—a consequence of the fine structure present in both the experimental data and the calculated $\chi^{(0)}$; for these frequencies, the lack of sensitivity of the loss spectrum to the effects of correlation is also a factor.
[25] W. Hanke and L. J. Sham, Phys. Rev. Lett. **33**, 582 (1974); Phys. Rev. B **21**, 4656 (1980).
[26] W. Schülke *et al.*, Phys. Rev. B **52**, 11 721 (1995), have estimated the LFF for Si by adjusting the position of the loss peak for jellium.