Dynamic Structure Factor of Electrons in Li by Inelastic Synchrotron X-Ray Scattering

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The dynamic structure factor, $S(\vec{q},\omega)$, of single-crystal Li exhibits a strong anisotropy of peak position and peak dispersion. For $q > q_c$ (q_c is the plasmon cutoff vector), at least the anisotropy of one peak position in $S(\vec{q},\omega)$ can be attributed to zone-boundary collective states within the limits of a one-reciprocal-lattice-vector model. Therefore, the double-peak structure of $S(\vec{q},\omega)$ for $q > q_c$ seems not to be a universal property of the strongly correlated electron gas.

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The dynamic structure factor, $S(\vec{q},\omega)$, for electrons of simple metals, above all for $q > q_c$ ($\vec{q}_c$ = plasmon cutoff vector), is far from being understood theoretically, even when the metal is approximated by a homogeneous electron gas. But also the experimental situation has been rather confusing so far: In the case of inelastic electron-scattering experiments, multiple scattering can obscure the spectra to a large extent. Thus it has become a matter of controversy to what extent the spectra beyond q_c show deviations of $S(\vec{q},\omega)$ from free-electron random-phase approximation (RPA).[1,2] Inelastic x-ray scattering, on the other hand, does not suffer from multiple scattering that much. But so far, the energy resolution and/or the statistical accuracy of the x-ray measurements has been rather poor. Nevertheless, some very interesting features of $S(\vec{q},\omega)$ have been revealed for $q > q_c$: (1) the persistence of a plasmonlike peak into the particle-hole-continuum[3-5]; (2) a nearly zero dispersion or possibly a negative dispersion of this peak[3-5]; (3) a second peak (or shoulder) which behaves more RPA-like with respect to its dispersion.[4,5] Since, for different metals and different crystallographic orientation of $\vec{q}$, this double-peak structure has been found to be similar when scaled according to electron gas parameters, it seems obvious to think of it as a general feature of a strongly correlated electron gas.[4] This conclusion has found support from weak-pseudopotential calculations,[6] which have estimated the band-structure effects to modify the free-electron spectra of simple metals by only a few percent. These two points have prompted a lot of theoretical investigations, which in some cases[7,8] have been successful in reproducing the double peak within the limits of a homogeneous-electron-gas approximation, whereas others[9-11] have failed in finding this special structure. On the other hand, a full band-structure calculation of the dynamic structure factor for $q > q_c$,[12] so far the only one for simple metals, has revealed a double-peak structure within the limits of RPA, stressing that weak-pseudopotential calculations[6] underestimate band-structure effects. Therefore, an experimental and theoretical reinvestigation of $S(\vec{q},\omega)$ for simple metals seems to be indispensable. In this context, inelastic x-ray scattering measurements, which utilize the advantages of synchrotron radiation, should provide the decisive experimental improvements and could remove all former shortcomings of x-ray methods when compared with electron methods. Following this line, this Letter presents the first synchrotron radiation measurements of $S(\vec{q},\omega)$ for Li. Because of the much-improved energy resolution and signal-to-background ratio, these measurements show that the position and strength of the double peak in $S(\vec{q},\omega)$ are strongly dependent on the orientation of the transferred momentum $\hbar\vec{q}$. Therefore, the origin of this special structure seems to be at least partly ion-electron interaction. Of course, the electrons cannot be simply represented in terms of a mean-field model. This will be confirmed in this Letter by demonstrating that our experimental results fit much better on a local-field-corrected homogeneous electron gas calculation than on a mean-field one.

Within the limits of first-order perturbation theory, the double differential cross section (DDCS) $d^2\sigma/d\omega d\Omega$ for inelastic x-ray scattering is directly related to $S(\vec{q},\omega)$ via

$$d^2\sigma/d\omega d\Omega = (\vec{e}_0\cdot\vec{e}\,')^2 r_0^2(\omega'/\omega_0)S(\vec{q},\omega), \quad (1)$$

where $\vec{e}$ and $\vec{e}\,'$ are the polarization vectors, $\hbar\omega_0$ and $\hbar\omega'$ are the energies of the incoming and scattered x-rays, respectively and r_0 is the classical electron radius.

The DDCS was measured by use of a spherically bent (333) Si-crystal spectrometer in nearly back-

Bragg-reflection geometry for analysis of the scattered beam, in connection with a (400) Si-double-crystal monochromator which provides $\simeq 2\times10^9$ photons $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ of $E_0 = 5.95$ keV within a relative bandpass $\Delta E/E_0 = 2\times10^{-4}$ at the scattering sample taken from the white synchrotron radiation beam of DORIS II (3.7 GeV, 50 mA). More details of the spectrometer performance are given elsewhere.[13] Further data of the measurements are as follows: Overall energy resolution of the spectra [full width at half maximum (FWHM) of the Rayleigh line] = 1.35 eV; the scattering vector $\vec{q}$ is fixed at $\pm 5\times10^{-2}q$; signal (peak of the inelastically scattered spectrum) -to-background ratio = 100; statistical accuracy in the inelastic peak = 1%. The steps of data processing are the following: (1) A linear background is subtracted. (2) The Rayleigh line is removed under the assumption that it is symmetric and is superimposed by the inelastic spectrum only in its low-energy half. Since the Rayleigh line is 7 to 12 times higher than the peak of the inelastic spectrum, the separated inelastic spectrum is less reliable in its initial part between 0 and 2 eV (only dotted lines in Fig. 1). (3) The measured DDCS's were brought to an absolute scale by means of the following well-known sum rule

$$\int_{-\infty}^{+\infty} S(\vec{q},\omega)\,\omega\, d\omega = \hbar q^2/2m. \qquad (2)$$

The Li single crystal, a plate of 3-mm thickness, which contains the [100], [110], and [111] directions in its surface, was etched to metallic luster before putting it into the evacuated (10^{-3} Torr) scattering chamber. After the measurement no appreciable oxide coating was found.

The influence of multiple scattering was tested by comparing in one case ($q = 0.77$ a.u.; $\vec{q}\parallel[100]$) the spectrum of a 3-mm-thick sample with that of a 6-mm-thick sample of the same orientation. The result is displayed in Fig. 1. Besides a small smearing of the fine structure, multiple scattering has no significant effect on the spectra.

The experimental results, as displayed in Fig. 1, are always compared both with a RPA $S(\vec{q},\omega)$ and a local-field–corrected $S(\vec{q},\omega)$, each calculated for the homogeneous electron gas of the Li metal. The RPA $S(\vec{q},\omega)$ was obtained by use of a generalization[14] of the Lindhard dielectric function $\epsilon_L(\vec{q},\omega + i/\tau)$, in order to express $S(\vec{q},\omega)$ by

$$S(\vec{q},\omega) = (\hbar q^2/4\pi^2 e^2 n)\,\mathrm{Im}\,\epsilon_L^{-1}(\vec{q},\omega + i/\tau), \qquad (3)$$

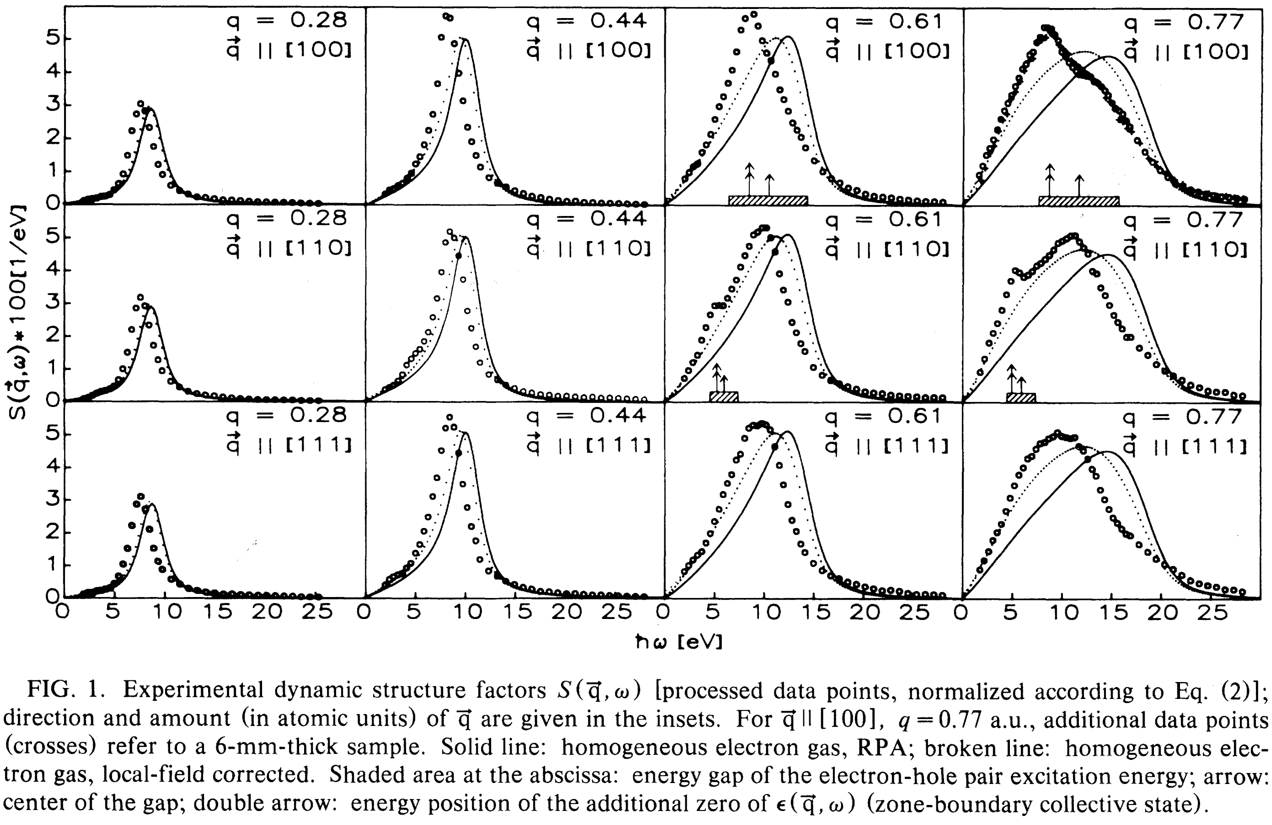

FIG. 1. Experimental dynamic structure factors $S(\vec{q},\omega)$ [processed data points, normalized according to Eq. (2)]; direction and amount (in atomic units) of $\vec{q}$ are given in the insets. For $\vec{q}\parallel[100]$, $q = 0.77$ a.u., additional data points (crosses) refer to a 6-mm-thick sample. Solid line: homogeneous electron gas, RPA; broken line: homogeneous electron gas, local-field corrected. Shaded area at the abscissa: energy gap of the electron-hole pair excitation energy; arrow: center of the gap; double arrow: energy position of the additional zero of $\epsilon(\vec{q},\omega)$ (zone-boundary collective state).

where n is the electron density. The local-field corrected $S(\vec{q},\omega)$ was calculated for a homogeneous electron gas by using in (3)

$$\epsilon(\vec{q},\omega+i/\tau)-1 = \frac{\epsilon_L(\vec{q},\omega+i/\tau)-1}{1-G(\vec{q})[\epsilon_L(\vec{q},\omega+i/\tau)-1]}. \tag{4}$$

The lifetime τ was fitted to the FWHM of the experimental spectra for $q=0.28$ a.u.; the static correction factor $G(\vec{q})$ is that of Vashishta and Singwi.[15] All theoretical curves are convoluted with the experimental resolution function, which can be read from the FWHM of the Rayleigh line.

In Fig. 1 processed experimental data for typical values of q are displayed together with the corresponding homogeneous–electron-gas curves. The experimental results are discussed mainly for $q > q_c$ ($q_c \approx 0.51$ a.u. for free-electron RPA).

For $q < q_c$ well-established plasmon peaks are visible, whose loss energy for $q=0.28$ a.u. is smaller by 1.1 eV than the electron-gas RPA value, independent of the $\vec{q}$ orientation. This indicates a strong influence of intraband transitions on the plasma resonance. Additionally the dispersion of the plasma resonances seems to be anisotropic.

The most important experimental results are those for $q > q_c$, which can be summarized as follows: (1) The fine structure of the $S(\vec{q},\omega)$ spectra depends strongly on the crystallographic orientation of $\vec{q}$ both when position and dispersion of peaks (or shoulders) are concerned. (2) Whenever two peaks can be discerned, one of them has nearly zero dispersion {see the peak (or shoulder) near $\omega=5$ eV for $\vec{q}\parallel[110]$ and the peak near $\omega=8.5$ eV for $\vec{q}\parallel[100]$}. (3) The second peak exhibits dispersion but does not follow the RPA peak with respect either to its position or to its dispersion. The local-field–corrected $S(\vec{q},\omega)$ of the homogeneous electron gas is closer to the second experimental peak but obviously cannot allow for its evident anisotropic position.

Mainly the orientation dependence of the first peak position in the experimental $S(\vec{q},\omega)$ spectra for $q > q_c$ gives strong evidence that a band-structure effect is the origin of the double-peak structure rather than a universal property of the correlated electron gas. This idea is supported by the following semiquantitative interpretation of the position and (zero) dispersion of the first peak in the [110] and [100] $S(\vec{q},\omega)$ spectra for $q > q_c$, which follows the one-reciprocal-lattice-vector model of Foo and Hopfield.[16] Within the limits of this model, the lattice periodicity is reduced to only one reciprocal lattice vector $\vec{G}$, so that the corresponding $\vec{G}$th Fourier coefficient $V_{\vec{G}}$ of the ion potential gives rise to a gap of width $2V_{\vec{G}}$ in the electron-hole pair excitation energy $\omega(\vec{k},\vec{q})$, when one starts with a Bloch state $|\vec{k}\rangle$ and uses $\vec{q}\parallel\vec{G}$. Therefore, an additional zero of the longitudinal dielectric function $\epsilon(\vec{q},\omega)$, the so-called zone-boundary collective state (ZBCS), exists within a range of width $2V_{\vec{G}}/\hbar$ around $\omega=\omega_{\vec{G}}(\vec{q}) = (-\hbar/2m)q(q-G)$. This zero gives rise to an additional peak in $S(\vec{q},\omega)$ near $\omega_{\vec{G}}(\vec{q})$, which should be visible in the spectra in spite of the appreciable oversimplification of the model. For $\vec{q}\parallel[100]$ the position of $\omega_{200}(\vec{q})$ is indicated in Fig. 1 by an arrow symmetrically surrounded by an energy range whose width is assumed to be equal to the relevant energy gap $\Delta E(H) \equiv E(H_1)-E(H_{15})$ of an energy-band calculation,[17] which provides $\Delta E(H)=7.9$ eV. For $\vec{q}\parallel[110]$ the position of $\omega_{110}(\vec{q})$ is also indicated in Fig. 1. The surrounding energy range is $\Delta E(N)=E(N_1)-E(N_1')=2.8$ eV.[17] The position of the additional zeros of $\epsilon(\vec{q},\omega)$ (ZBCS's) within the energy range of width $2V_{\vec{G}}$ has been calculated with the formalism of Foo and Hopfield[16] with $2V_{\vec{G}}=\Delta E(H)$ for $\vec{q}\parallel[100]$, and $2V_{\vec{G}}=\Delta E(N)$ for $\vec{q}\parallel[110]$. These positions are indicated by double arrows in Fig. 1. Their coincidence with the first (zero dispersion) peak of the experimental spectra is evident. For $\vec{q}\parallel[111]$ the ZBCS is outside the electron-hole pair continuum.

In summary, one has to come to the conclusion that the dynamical structure factor $S(\vec{q},\omega)$ of electrons in the Li metal can be represented sufficiently neither in terms of a random phase approximated nor completely in terms of a local-field–corrected homogeneous electron gas. Intrinsic structures of $S(\vec{q},\omega)$ (double peak) apparently have their origin in the band structure, and can be understood partly as due to gaps in the electron-hole pair excitation spectra for transitions which end on states near the zone boundary (ZBCS's).

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