Dynamic Structure Factor of Diamond and LiF Measured Using Inelastic X-Ray Scattering

W. A. Caliebe*
Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

J. A. Soininen† and Eric L. Shirley
Optical Technology Division, Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

C.-C. Kao
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

K. Hämäläinen
Department of Physics, University of Helsinki, POB 9, FIN-00014, Helsinki, Finland
(Received 9 September 1999)

The dynamic structure factors $S(\vec{q},\omega)$ of diamond and LiF have been measured using inelastic x-ray scattering. The experimental data are compared to results of *ab initio* calculations, which take into account the interaction of the excited electron with the remaining hole. In diamond, the vicinity of the indirect band gap and its momentum dependence are studied. In LiF, a larger energy range, which covers the fundamental exciton, the plasmon, and several interband transitions, is investigated. Calculations and measurements agree quite well and emphasize the need to properly include the interaction of the excited electron in the conduction band with the hole in the valence band.

PACS numbers: 71.15.Cr, 78.70.Ck

The dynamic structure factor $S(\vec{q},\omega)$ of valence electrons in condensed matter is the Fourier transform in space and time of the time-dependent density-density correlation function. $S(\vec{q},\omega)$ can be measured on an absolute scale by inelastic scattering of x rays (IXS) or electrons (electron energy loss spectroscopy, EELS). So far, mostly simple metals like Be, Li, Na, or Al [1,2] have been studied with IXS. The experimental results were compared to calculations based on jellium and model pseudopotential band-structure calculations. Correlation effects beyond the random-phase approximation (RPA) were treated with a local-field factor. The agreement was fairly good for small momentum transfers, and some fine structure at intermediate momentum transfers was attributed to band-structure effects. First-principles calculations by Fleszar *et al.* and Quong *et al.* [3] supported this picture. By destroying the long-range order by melting the sample, this fine structure almost disappeared, which was used as an argument for the explanations based on band-structure effects. Band-structure effects also cause a negative dispersion of the plasmon in Cs [4].

Here we have studied insulators where band-structure effects are much stronger. Comparison with theory uses *ab initio* calculations of $S(\vec{q},\omega)$ including the electron-hole interaction. A similar scheme has yielded the imaginary part of the macroscopic ($\vec{q} = 0$) dielectric function $\epsilon_2(\omega)$ in semiconductors and insulators [5]. Now the method has been extended to calculation of $\epsilon_2(\vec{q},\omega)$, and $S(\vec{q},\omega)$ via the fluctuation-dissipation theorem [6].

We wish to observe energy *and* momentum of the indirect band gap in diamond near $0.75\Gamma X$ and $\hbar\omega = 5.5$ eV and to measure $S(\vec{q},\omega)$ between 0.35 and 2.3 Å^{-1} (0.23 and 1.49 ΓX) and between 0 and 35 eV in LiF along the (001) direction. The experimental setup is described, there is a short description of the theoretical calculations, and the experimental data are presented. A comparison of theory and experiment follows.

We have used inelastic x-ray scattering to determine $S(\vec{q},\omega)$, which is simply proportional to the double-differential scattering cross section. The experiments were performed at beam line X21 at the National Synchrotron Light Source, Brookhaven National Laboratory. X rays of the wiggler are monochromatized and focused by a cylindrically bent and asymmetrically cut Si(220) monochromator. The energy resolution is 0.6 eV at 7.93 keV, and the flux is 2×10^{11} photons/s. Scattered photons are energy-analyzed by a spherically bent Si(444) crystal at a fixed scattering angle of 85.8° and diffracted into a Si(Li) detector. Energy transfer is measured by tuning incident energy, thus maintaining the energy resolution. The momentum resolution (FWHM) is dominated by the size of the analyzer crystal and varies between 0.5 Å^{-1} at $q = 0.3$ Å^{-1} (0.23 ΓX in LiF) and 0.3 Å^{-1} at $q = 2.3$ Å^{-1} (1.49 ΓX in LiF). To study diamond, the size of the analyzer was reduced to obtain a momentum resolution of 0.1 Å^{-1}. The momentum transfer depends on the scattering angle 2Θ as $q \approx 4\pi/\lambda \sin(\Theta)$, where λ is the wavelength of the radiation, and it is nearly constant within our energy range of interest. The overall energy resolution, including the energy width of the incident beam, contributions from the size of focus, and the energy resolution of the

crystal analyzer, is 0.7 eV. The experimental setup is described in detail elsewhere [7,8].

The diamond crystal used in the experiment had dimensions $4 \times 4 \times 0.5$ mm^3. For LiF, several 0.5 mm thick crystals were used with other dimensions varying between 5×10 and 10×10 mm^2. The crystal surfaces were in all cases (001) surfaces. The widths of the rocking curves were limited by the divergence of the incident beam ($\approx 0.08°$). Samples were measured in a transmission geometry to reduce the influence of the source size on the analyzer energy resolution.

The theoretical calculations were made with a scheme that is an extension of Ref. [5]. The technique calculates $\epsilon_2(\vec{q}, \omega)$ using an effective Hamiltonian obtained from the Bethe-Salpeter equation. The effective Hamiltonian includes a one-particle term, a "direct" term, which describes the attractive interaction between the electron and the hole, and the accompanying repulsive "exchange" term. One-particle eigenstates were used as a basis for describing the electron-hole pair wave function and were calculated using the pseudopotential method [9] and the local-density approximation (LDA) [10]. Single-particle energies were corrected based on *GW* calculations [11]. A bare Coulomb interaction was used for the "exchange" term and the "direct" term was screened using the Levine-Louie-Hybertsen model [12]. Phonon effects were neglected. Unlike in Ref. [5], now the electron-hole pair has a finite momentum, and the matrix elements $\langle i, j; \vec{k}|P|0\rangle$ [Eq. (19) in Ref. [5]] involve the density fluctuation operator $P = \hat{\rho}^{\dagger}_{\vec{q}}$. We found that a finer $\vec{k}$ grid is needed to describe the electron-hole pair at finite q.

Experimental data (open circles) and results of theoretical calculations (solid and broken lines) are shown in Figs. 1 to 3; measurement uncertainties are smaller than the symbol size or given by small vertical lines. The maximum error of the energy scale is 0.2 eV. We used the f sum rule as described by Schülke *et al.* [13] to normalize experimental data for diamond between 5 and 140 eV. Theoretical data were automatically correctly normalized. In LiF, we could not use the f sum rule for normalization, because we measured oscillator strength only up to 65 eV, so we scaled experiment to theory.

For medium momentum transfers, experiment and theory show a similar behavior in diamond: after a small rise at about 5.5 eV (see Fig. 1) the intensity varies little until a steep rise at about 11 eV (see Fig. 2). The shape of the first steep rise in the experimental spectra varies little between 1.26 ΓX and 1.64 ΓX. In the theory, this first rise shifts to lower energy transfer and becomes less steep for both models, but the overall agreement is much better when including the electron-hole interaction. The q dependence of the intensity of the first rise near ≈ 5.5 eV is almost identical in experiment and theory, and such agreement can be achieved only by including the electron-hole interaction in the theory. Also, experiment and theory both indicate that the band gap is not observed in the first

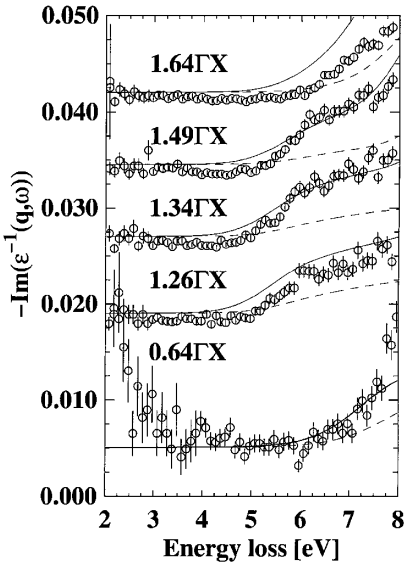

FIG. 1. $-\mathrm{Im}[\epsilon^{-1}(\vec{q}, \omega)]$ of diamond near the band gap as a function of momentum transfer in the ΓX direction. The circles are experimental data, the solid lines are theoretical data calculated including the electron-hole interactions in the final state, and the broken lines are theoretical data calculated without the electron-hole interactions. The intensities for all spectra are in absolute values on the same scale. Only a constant background is added to the theoretical data.

Brillouin zone at $q = 0.64$ ΓX, but instead in the second Brillouin zone at $q = 1.34$ ΓX. This is due to the symmetry of the Bloch states. The valence band maximum (VBM) is at Γ, and the conduction band minimum (CBM)

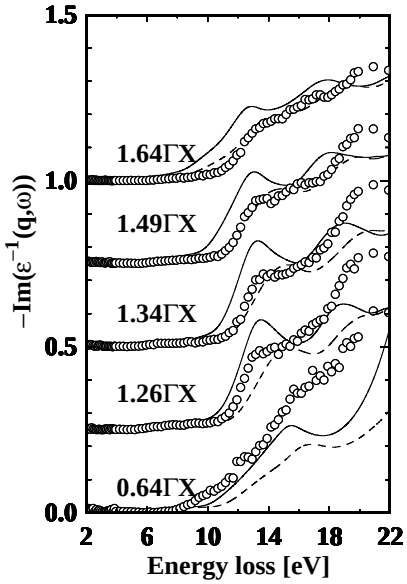

FIG. 2. $-\mathrm{Im}[\epsilon^{-1}(\vec{q}, \omega)]$ of diamond from 2 to 22 eV as a function of momentum transfer in the ΓX direction. The symbols and constant background are the same as in Fig. 1. This energy range covers the first low-lying transitions including the band gap. The plasmon, however, is observed at approximately 30 eV.

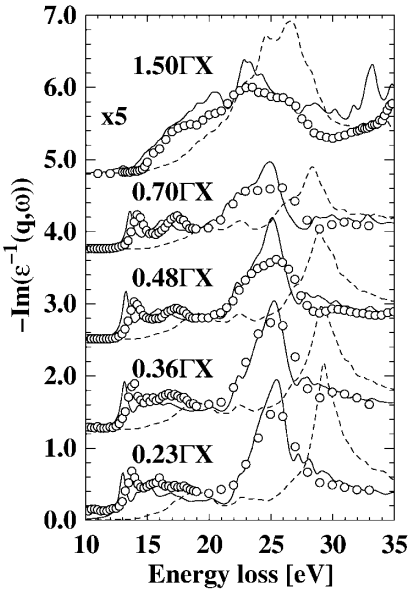

FIG. 3. $-\mathrm{Im}[\epsilon^{-1}(\vec{q},\omega)]$ of LiF as a function of momentum transfer in the ΓX direction. The symbols are the same as in Fig. 1.

is at approximately 0.75 ΓX on the Δ line (Γ to X; see, e.g., Refs. [11,14,15]). Near the VBM, a Bloch state has the form $|\psi_{n\vec{k}}(\mathrm{VBM})\rangle \sim |\phi_{2p_\alpha,\tau_1}\rangle - |\phi_{2p_\alpha,\tau_2}\rangle$. Here α is a Cartesian direction, and $\phi_{2s,\tau}$ and $\phi_{2p_\alpha,\tau}$ are atomic states on one of the two sites τ in the unit cell. Near the CBM, Bloch states have the form

$$|\psi_{n'\vec{k}'}(\mathrm{CBM})\rangle \sim \sum_{\tau=\tau_1,\tau_2} \exp(i\vec{k}'\cdot\vec{\tau})\,[A(\vec{k}')|\phi_{2s,\tau}\rangle + B(\vec{k}')\,|\phi_{2p_\alpha,\tau}\rangle], \quad (1)$$

and α is the Cartesian axis of the Δ line parallel to $\vec{q}$. Analogous orbitals on equivalent sites are combined with opposite signs at the VBM and with indicated phases at the CBM. This induces a cancellation so that the transition matrix element $\langle\psi_{n'\vec{k}'}(\mathrm{CBM})\,|e^{i\vec{q}\cdot\vec{r}}|\psi_{n\vec{k}}(\mathrm{VBM})\rangle$ is small for $\vec{q} = \vec{k}' \approx 0.75\ \Gamma X$ and $\vec{k} \approx 0$ and constructive interference for $\vec{q} = \vec{k}' + \vec{G} \approx 1.25\ \Gamma X$, where $\vec{G}$ is the reciprocal-lattice vector at 2 ΓX, and CBM states at $\vec{k}' \approx -0.75\ \Gamma X$ are probed [16].

In absorption and reflectivity measurements the momentum of the absorbed or reflected photon is too low to provide a large enough momentum transfer to observe such an indirect band gap. When such a gap is observed the necessary momentum is provided by a phonon, so that three particles are involved in the transition (photon, phonon, and electron). The cross section is still very low and the experiment cannot determine the momentum of the phonon even within units of the Brillouin zone. That can be done only with scattering methods such as IXS, in which energy and momentum are transferred by the scattered particle.

In LiF, we have studied and compared the energy loss spectra between 10 and 35 eV. A similar energy and smaller momentum range have been studied with EELS by Fields *et al.* [17]. The main features in the spectra (see Fig. 3) are the very narrow exciton around 14 eV and the nominal plasmon around 25 eV [17,18]. Some intermediate transitions, which are lower in intensity, are also clearly observed. At energies above 35 eV, core hole excitations of F 2*s* electrons are observed (calculated at 33 eV), and at 61 eV Li 1*s* electrons are excited.

The difference between the theoretical models with/without the electron-hole interaction is significant. Neglecting the interaction, all energies of the peaks are higher by $\approx$3 eV, because the attraction pulls states down in energy, and the exciton is not reproduced, because an exciton is a bound electron-hole pair. Comparing the experiment with theory, it is obvious that a proper treatment of the interaction of the electron with the hole is necessary. The theoretical value for the exciton energy is too low by $\sim$0.6 eV, which is large compared to the width of the exciton of 0.5 eV, but is acceptable for *ab initio* calculations that include no adjustable parameters.

The plasmon is reproduced as well. Its energy and width as a function of momentum transfer agree very well for the experimental data and the calculations including the interaction of the excited electron with the hole. Calculations by Michiels *et al.* [19] reproduced the energy and intensity of the plasmon as a function of momentum transfer quite well, but the calculated width was too small. Between the exciton and the plasmon, smaller peaks are modeled well as interband transitions that evolve with momentum transfer. For the lowest momentum transfer, both experiment and theory including electron-hole interaction show peaks at 15 and 18 eV, with the 15 eV one higher in intensity. Increasing the momentum transfer, the two peaks merge into one peak near 18 eV. Increasing the momentum transfer even further, this peak narrows, indicating that the transitions move closer in energy. Again, theory without electron-hole interactions is different.

To summarize, we measured the dynamic structure factor $S(\vec{q},\omega)$ of LiF in the (001) direction and the indirect band gap in diamond and compared the experimental results to *ab initio* calculations. The band gap in diamond is observed only in the second Brillouin zone, a result reproduced by theory, and neglecting electron-hole interactions leads to less accurate results. In LiF, the agreement between experiment and theory is good only if the electron-hole interaction is included. Its neglect results in energies of transitions that are too high and a complete absence of the experimentally observed exciton peak and fine structure.

This demonstrates the study of the band structure and especially an indirect band gap with IXS. Here only simple (regarding electronic structure) compounds and light elements like diamond or LiF were studied. With the increasing availability of highly monochromatic x-ray beam with higher energies, the study of heavier and more complex systems becomes more feasible. One application could be

the study of high-T_c superconductors with IXS. The required energy resolution would be ~5 meV, which is easily achieved with current techniques [20]. As in the present case, the cross section is very small, and absorption by the sample is larger, so that this experiment is not easily performed [21].

We thank F. Sette for loaning his Si(444) crystal analyzer. The National Synchrotron Light Source is supported by the Department of Energy under Contract No. DE-AC02-98CH10886. K. H. is supported by the Academy of Finland (7349/40732). J. A. S. is supported by the Väisälä Fund and the Academy of Finland (45226).

*Permanent address: National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973.

†Permanent address: University of Helsinki, Department of Physics, POB 9, FIN-00014, Helsinki, Finland.

[1] W. Schülke, H. Nagasawa, and S. Mourikis, Phys. Rev. Lett. **52**, 2065 (1984); W.Schülke, H. Nagasawa, S. Mourikis, and P. Lanzki, Phys. Rev. B **33**, 6744 (1986); J. P. Hill *et al.*, Phys. Rev. Lett. **77**, 3665 (1997).

[2] W. Schülke, H. Nagasawa, S. Mourikis, and A. Kaprolat, Phys. Rev. B **40**, 12 215 (1989); W. Schülke, H. Schulte-Schrepping, and J. R. Schmitz, Phys. Rev. B **47**, 12 426 (1993); C. Sternemann, A. Kaprolat, and W. Schülke, Phys. Rev. B **57**, 622 (1998).

[3] A. A. Quong and A. G. Eguiluz, Phys. Rev. Lett. **70**, 3955 (1993); A. Fleszar, A. A. Quong, and A. G. Eguiluz, Phys. Rev. Lett. **74**, 590 (1995).

[4] F. Aryasetiawan and K. Karlsson, Phys. Rev. Lett. **73**, 1679 (1994).

[5] L. X. Benedict and E. L. Shirley, Phys. Rev. B **59**, 5441 (1999).

[6] D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (W. A. Benjamin, New York, 1966).

[7] K. Hämäläinen, M. Krisch, W. Caliebe, and J. B. Hastings, Rev. Sci. Instrum. **66**, 1525 (1995); C.-C. Kao, K. Hämäläinen, M. Krisch, D. P. Siddons, T. Oversluizen, and J. B. Hastings, Rev. Sci. Instrum. **66**, 1699 (1995).

[8] W. A. Caliebe, Ph.D. thesis, University of Kiel, 1997.

[9] For a review, see W. E. Pickett, Comput. Phys. Rep. **9**, 115 (1989).

[10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[11] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); E. L. Shirley, L. J. Terminello, J. E. Klepeis, and F. J. Himpsel, Phys. Rev. B **53**, 10 296 (1996).

[12] Z. H. Levine and S. G. Louie, Phys. Rev. B **25**, 6310 (1982); M. S. Hybertsen and S. G. Louie, Phys. Rev. B **37**, 2733 (1988).

[13] W. Schülke, U. Bonse, H. Nagasawa, A. Kaprolat, and A. Berthold, Phys. Rev. B **38**, 2112 (1988).

[14] G. S. Painter, D. E. Ellis, and A. R. Lubinsky, Phys. Rev. B **4**, 3610 (1971).

[15] J. R. Chelikowsky and S. G. Louie, Phys. Rev. B **29**, 3470 (1984).

[16] We do not consider the difference of the momentum transfer of the band gap between our experiment ($0.65\Gamma X$) and published values ($0.75\Gamma X$) to be a serious problem, as the conduction and valence bands are both very flat in the vicinity of the band gap. The differences between the experimental spectra at $q = 1.26$ and $q = 1.34\Gamma X$ are minor.

[17] J. R. Fields, P. C. Gibbons, and S. E. Schnatterly, Phys. Rev. Lett. **38**, 430 (1977).

[18] The calculated real part of the dielectric function ϵ_M^1 crosses zero around 25 eV for momentum transfers 0.23 to $0.46\Gamma X$, and it is close to zero for $q = 0.72\Gamma X$.

[19] J. J. M. Michiels, L. Hedin, and J. E. Inglesfield, Phys. Rev. B **50**, 11 386 (1995).

[20] E. Burkel, *Inelastic Scattering of X-Rays with Very High Energy Resolution* (Springer Verlag, Berlin, 1991); R. Verbeni, F. Sette, M. H. Krisch, U. Bergmann, B. Gorges, C. Halcoussis, K. Martel, C. Masciovecchio, J. F. Ribois, G. Ruocco, and H. Sinn, J. Synchrotron Radiat. **3**, 62 (1996); M. Schwoerer-Boehning, A. T. Macrander, P. M. Abbamonte, and D. A. Arms, Rev. Sci. Instrum. **69**, 3109 (1998).

[21] M. Altarelli (private communication).