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Ab initio calculations of the dynamic response of beryllium

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We present results from *ab initio* calculations of the full inverse dielectric matrix of beryllium, from which we obtain the dynamic scattering cross section. This is shown to be in excellent agreement with recent inelastic x-ray-scattering experiments, both in overall shape and in precise details of the fine structure. As the calculations have been performed entirely within the random-phase approximation, this presents conclusive evidence that band-structure effects are responsible for the observed structure.

In recent years, high-resolution studies[1] of the x-ray-scattering cross section of light materials have been made possible by the advent of brighter x-ray sources and more-efficient detectors. By applying the fluctuation-dissipation theorem,[2-4] direct observations of the dynamic density-density response function are possible. This response function is of basic importance in the theory of quasiparticle excitations and many-body theories in general.

Despite this wealth of experimental data, there have been surprisingly few first-principles calculations of the dynamic scattering cross section $S(\mathbf{q},\omega)$, which include the full effects of the crystal lattice. The original interest in these systems was prompted by the experimental results of Platzman and co-workers.[5-8] These early experiments were performed at a much lower resolution than the later work of Schülke *et al.*,[9] and their deceptionally smooth nature and universal double-peak feature encouraged a wealth of theoretical work which attempted to explain the features in terms of electron-electron interactions within a homogeneous electron gas.

As the simple random-phase approximation (RPA) for a homogeneous system cannot produce the observed fine structure, the main thrust of the theoretical work was involved in going beyond the RPA. Green and co-workers[10,11] achieved some success by a perturbative approach, noting that their fine structure arose from terms involving electron-electron scattering. They managed to show some correlation between their results and experiment for the main peak and the dip, but the energy position of the features was rarely in agreement. They noted that the data of Platzman and Eisenberger[8] for beryllium contained a normalization inconsistency and speculated that this may be due to lattice effects. Mukhopadhyay, Kalia, and Singwi[12] incorporated lifetime effects of the electron-hole pair via the imaginary part of the self-energy. The resulting fine structure is appreciably smaller in magnitude than its experimental counterpart but, for the case of aluminum,[13] occurs at approximately the correct energies.

The universal nature of the double-peak structure dissuaded many authors from considering crystal lattice effects as the source of the fine structure. However, the relatively recent experimental results of Schülke *et al.*[9] and their use of a simple two-band model to explain at least the orientationally dependent fine structure in terms of lattice-induced excitation gaps, seem to present a compelling argument for the band-structure origins of the structure. Previously, Oliveira and Sturm[14] had performed a similar calculation by "folding down" the dielectric response matrix to a two-band model, but had argued that lifetime effects were so strong at the Brillouin-zone boundary that there was no evidence for a double-peak structure.

In beryllium the presence of orientationally dependent fine structure and its strongly nonjelliumlike pseudopotential mean that band-structure effects are thought to play a large role. In this paper we show that fully incorporating band-structure effects within the RPA dramatically modifies the dynamic scattering cross section to such an extent that it accounts for all of the observed fine structure.

The fluctuation-dissipation theorem relates the scattering cross-section $S(\mathbf{q},\omega)$ to the density-density correlation function[15] of the scatterers. This function is in turn directly related to the inverse dielectric function $\epsilon^{-1}(\mathbf{x},\mathbf{x}'|\omega)$, so that[16]

$$S(\mathbf{q}+\mathbf{G},\omega)=\frac{1}{\pi}\frac{1}{\phi_q}\operatorname{Im}\{\epsilon^{-1}_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)\}\ ,$$

where $\phi_q=4\pi e^2/q^2$ is the Fourier transform of the Coulomb potential, and $\epsilon^{-1}(\mathbf{x},\mathbf{x}'|\omega)$ has also been Fourier transformed into a matrix $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$, where

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$\mathbf{G},\mathbf{G}'$ are reciprocal lattice vectors.

The central expression in our calculations is the independent-particle polarizability $\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$, which is given by[17,18]

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)=\frac{4}{\pi}\sum_{n,n',\mathbf{k}}\langle n',\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n,\mathbf{k}+\mathbf{q}\rangle \times\langle n,\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|n',\mathbf{k}\rangle \times\frac{f_0(E_{n,\mathbf{k}+\mathbf{q}})-f_0(E_{n',\mathbf{k}})}{E_{n',\mathbf{k}}-E_{n,\mathbf{k}+\mathbf{q}}+\hbar\omega+i\eta}\,, \qquad (1)$$

where n and n' are summed over all the bands at the point in reciprocal space $\mathbf{k}$, and $\mathbf{k}$ is summed over the first Brillouin zone. f_0 is the Fermi-Dirac distribution function, and $|n,\mathbf{k}\rangle$ and $E_{n,\mathbf{k}}$ are a suitable set of one-electron wave functions and eigenvalues. Within the RPA (time-dependent Hartree theory), $\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ is related to the inverse dielectric matrix through the matrix equation $\epsilon^{-1}(\mathbf{q},\omega)=1+V_c(1-\chi^0V_c)^{-1}\chi^0$. A mathematically equivalent, but computationally more efficient, method has been formulated by Quong and Eguiluz,[19] which overcomes the laborious band summation in Eq. (1).

We note in passing that a simple way to proceed beyond the RPA is to replace the second occurrence of V_c in the above expression with an effective potential $V_{\text{eff}}=V_c(\mathbf{x}-\mathbf{x}')+K_{\text{xc}}(\mathbf{x},\mathbf{x}')$, where K_{xc} is the functional derivative of the exchange and correlation potential, $K_{\text{xc}}(\mathbf{x},\mathbf{x}')=\partial V_{\text{xc}}(\mathbf{x})/\partial n(\mathbf{x}')$. This functional is usually approximated by that of an electron gas of density equal to the density at x, the so-called local-density approximation. We have included this correction term in several calculations but, as the differences were typically of the order of our estimated numerical error of 5%, we will present results at the RPA level alone in what follows.

The wave functions and band energies used in the evaluation of the above equations were generated by a self-consistent psuedopotential calculation. A norm-conserving pseudopotential[20] of Kerker type[21] was used to represent the Be^{2+} ions, which incorporated nonlinear core exchange-correlation corrections,[22] which significantly improve the calculated structural properties of hexagonal close-packed beryllium. We used the experimental values for the crystal structure of $c/a=1.568$ and $a=2.2858$ Å. The potentials and valence electronic wave functions were expanded in a plane-wave basis set containing all waves up to 24 Ry in energy. Brillouin-zone integrations were performed by sampling a grid of 432 points obtained by symmetrizing a $6\times6\times4$ Monkhorst-Pack[23] mesh. Our calculations were performed within the local-density-functional formalism using the Ceperley-Alder form[24] of the local-density approximation for the exchange-correlation potential.

The analytic structure of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ in the complex energy plane means that we cannot perform our calculations at exactly real energies due to the presence of a branch cut along the real axis. We must, therefore, calculate $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ at points close to the real axis in the complex plane, but with a finite imaginary energy part. One of the greatest limiting factors in these calculations must be computational expense. It is very costly to evaluate $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ very close to the real axis, as it requires a large number of bands and plane waves to achieve a given level of accuracy and convergence.

One method of circumventing this problem is to make use of the analytical structure of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ and represent it as a Taylor-series expansion[25] derived from function values evaluated further from the real axis. These relatively cheap function evaluations can then be used to continue to discrete $\mathbf{q}$ and ω points close to the real axis. Due to the smoother nature of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ at greater distances from the branch cut, the continued function values were of a similar accuracy to the explicitly calculated values. Indeed, tests have shown that the Taylor-series expansion converged more quickly, with respect to the number of plane waves used, than did the explicitly calculated function.

It is a well-known phenomenon that the numerical calculation of derivatives in terms of simple differencing of neighboring function values is a process subject to large and unpredictable error due to the amplification of small numerical errors in the calculation. We have circumvented this difficulty by taking advantage of the analytic nature of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ and Cauchy's expression for the derivative. We follow the work of Lyness and coworkers[26,27] and evaluate the contour integral numerically, using a circle of radius r, centered on z_0. We use $r=1.4$ eV, and have checked that the results are insensitive to varying r over two orders of magnitude. $\text{Im}\{z_0\}$ was chosen sufficiently large to give a useful radius of convergence, but not so large that a very-high-order Taylor expansion is needed to yield the structure in $S(\mathbf{q},\omega)$, which would cause numerical instability. Tests using explicitly calculated values show that a wide range of values of $\text{Im}\{z_0\}$ are suitable: we typically used 13 eV. By repeating this procedure with different values of $\text{Re}\{z_0\}$ we cover successive sections of the real energy axis. Making an appropriate change of variable and inserting the Taylor-series expansion of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$, we obtain, for each element of $\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ the Fourier expansion

$$r^n a_n=\frac{1}{m}\sum_{j=0}^{m-1}e^{-2\pi ijn/m}\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},z_0+re^{i2\pi j/m})\,,$$

where a_n is the nth-order derivative, and n runs from 0 to $m-1$. From the above, we see that the approximation requires m function values for its evaluation, which then yield $m-1$ derivatives. In our calculations we used a value of 10 for m. It should also be noted that, unlike the simple differencing methods, all the function evaluations contribute to the calculation of each derivative. For example, the first derivative which might normally be calculated with just two function evaluations, is here evaluated with ten, yielding much improved accuracy for the most important term in the Taylor-series expansion.

The fundamental expression, Eq. (1), contains explicit summations over bands and k points, and an implicit summation over the number of plane waves we use to approximate the true wave functions. Our calculations have shown that as few as 23 plane waves and 20 bands, which span an energy range of 64 eV, reproduce a

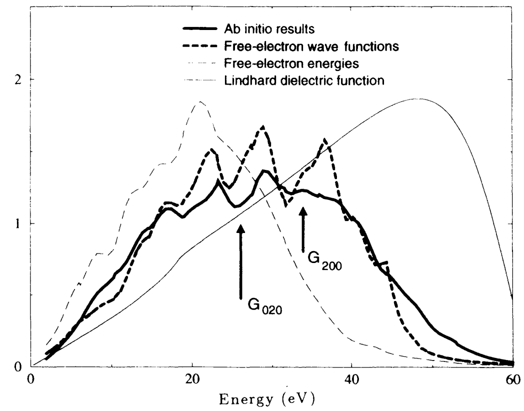

FIG. 1. Typical results for $S(\mathbf{q},\omega)$ in this case for $|\mathbf{q}|=1.119$ a.u.$^{-1}$ parallel to the 100 reciprocal lattice direction. The arrows indicate the positions of dips due to the G_{200} family of planes predicted by a simple model calculation (Ref. 9). Also shown are the equivalent calculations performed with either free-electron wave functions or energies instead of the beryllium ones.

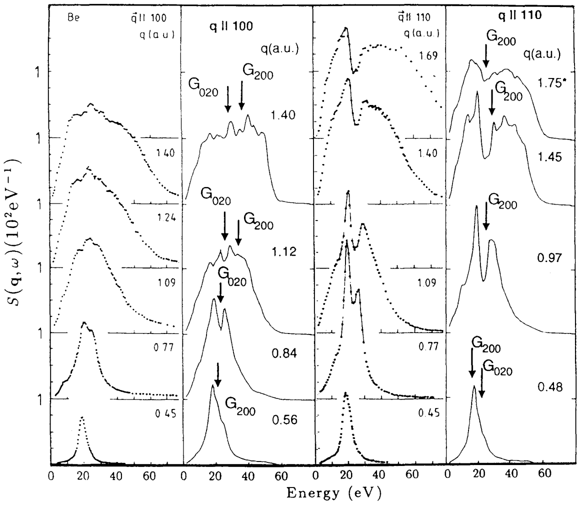

FIG. 2. Comparison of the experimental data of Schülke *et al.* (Ref. 9) (small dots) and theoretical calculations (smooth lines). It should be noted that, although the directions of the various q used are identical, the actual size of q is the closest possible match with the experimental value, so interpolation is necessary to compare some of the graphs. The arrows indicate the predicted positions of dips due to the various members of the G_{200} family of planes predicted by a simple model calculation (Ref. 9).

sufficiently converged $S(\mathbf{q},\omega)$ for our purposes (so that the peak positions are converged to within 0.5 eV). In order to test the dependence of our results on the number of k points in the summation (1), we also used a data set containing half our usual number of 432 k points in the Brillouin zone: this produced a maximum change of 7% in $S(\mathbf{q},\omega)$, which is of the order of our predicted error. The position and relative size of the fine structure remained essentially unaltered. By restricting ourselves to a discrete mesh of k points we also limit the values of $\mathbf{q}$ $(=\mathbf{k}-\mathbf{k}')$ we can use, and therefore in the graphs which follow the magnitude of $\mathbf{q}$ is the closest possible match with the experimental values for each direction of $\mathbf{q}$ coinciding with a prominent reciprocal-lattice vector.

We present our results in a similar way to those of Schülke *et al.*[9] which are, to our knowledge, the only experimental results of sufficient resolution. Figure 1 illustrates the general trends seen in our calculations. Our results are in good agreement with the experimentally observed ones, with both showing a shift in the weight of $S(\mathbf{q},\omega)$ to lower energies than predicted by the RPA for jellium. The dip is within 6% of that predicted by excitation gaps across Bragg planes in a simple two-band model,[9] in this case that arising from the G_{020} plane. Also marked is the predicted dip position for the G_{200} plane, and it is a general feature that the major components of the fine structure can be attributed to the dips created by these two Bragg planes. The simple model predicts gaps rather than dips because of its neglect of the other components of the crystal potential or the fact that beryllium has more than one conduction band.

Figure 2 shows both the observed and calculated $S(\mathbf{q},\omega)$ for the directions (100) and (110) in the hexagonal reciprocal space. While the positions of the predicted dips due to the G_{020} and G_{200} planes serve to show that much of the fine structure is generated by these two planes, it should also be remembered that these positions will be modified from the simple two-band model in the general case. Overall our calculations reproduce the energy dependence of the structure extremely well and it is only the distribution of weight into these features which differs from experiment.

In order to discern the exact origin of the fine structure in our calculations, we consider separately the contributions of the matrix elements and the energy denominators in (1). To do this we have repeated the calculation replacing first the wave functions $|n,\mathbf{k}\rangle$, and then the band energies $E_{n,\mathbf{k}}$, by their free-electron counterparts. This analysis is shown for $q=1.119$ a.u.$^{-1}$ in Fig. 1, and it is clear that it is the inclusion of the correct beryllium energy denominators which is the chief origin of the structure.

In conclusion, we have established that band-structure effects alone can account for all the fine structure in the dynamic scattering cross section of beryllium, most of which arises from nearly-free-electron modifications of the energy denominators arising from the G_{020} and G_{200} components of the lattice potential. Indeed, calculations[28,29] performed on aluminum, whose pseudopotential is considerably weaker than that of beryllium, have revealed that the observed double-peak structure in its $S(\mathbf{q},\omega)$ can also be attributed to crystal lattice effects. It would seem that the contribution of the pseudopotential in modifying the free-electron behavior of simple metals have been previously underestimated.

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