Inelastic electron scattering near the K edge in Be

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The energy- and momentum-dependent cross section for 200-keV electrons scattered from thin Be foils has been measured. For energy losses within 30 V of the K edge and for momentum transfers out to $q = 4$ Å^{-1} we compare the experimental results with a theoretical one-electron band-structure calculation which includes matrix elements. Within a few volts of the edge the results agree but then begin to deviate significantly at high energies. Many-electron excitations are proposed as a mechanism to partially account for these discrepancies.

When high-energy electrons are singly scattered from a thin foil of material, the energy lost by the scattered electron is a direct measure of the electronic-excitation spectrum of the system. As the angle of scattering is varied, the various matrix elements for transitions to these excited states will change in a simple way. In fact, it is well known that the cross section for scattering of high-energy electrons with momentum transfer q and energy transfer ω, is to a very good degree of approximation given by

$$\frac{d\sigma}{d\Omega\, d\omega} = \frac{r_0^2}{(q\hbar/mc)^4\pi} S(\vec{q}, \omega) , \tag{1}$$

where $r_0^2 = e^4/m^2c^4$, and neglecting exchange contributions

$$S(\vec{q}, \omega) = \sum_{i,f} \left| \langle f | \sum_j e^{i\vec{q}\cdot\vec{r}_j} | i \rangle \right|^2 \delta(E_f + E_i - \hbar\omega) . \tag{2}$$

The momentum transfer $\vec{q}$ is quite accurately determined by the scattering angle, i.e.,

$$q = (2p/\hbar)\sin(\tfrac{1}{2}\theta) . \tag{3}$$

When the initial and final states in Eq. (2) are in the valence and conduction bands, respectively, $S(\vec{q}, \omega)$ reflects, at small q, the collective modes of the electronic system. In particular, the plasmon to a great extent dominates such a spectrum. If $|i\rangle$ is a deep-core state, then $S(\vec{q}, \omega)$ exhibits an absorption edge whose energy is determined by the binding of the core state and whose shape reflects the density of low-lying unoccupied states multiplied by transition matrix elements of the density operator

$$\rho_q = \sum_j e^{i\vec{q}\cdot\vec{r}_j} ,$$

where j is a summation index over all electrons. In this case, the matrix elements of the density operator reduces, in the one-electron or Hartree-Fock approximation, to a sum of matrix elements squared of $e^{i\vec{q}\cdot\vec{r}}$ between the filled orbitals and empty conduction-band states. This is the case we will consider.

Recently, there has been considerable interest in the behavior of edge spectra.[1,2] The emphasis has been on high-resolution studies very near threshold, where the singular behavior of the low-lying density of many-electron states plays an important role. In this low-resolution study, we focus on the core spectrum over a broad energy and momentum range and compare it with a one-electron band-structure calculation.

We have measured the inelastic-scattering cross section of 200-keV electrons scattered from 400-Å Be films for momentum transfers $q = 0$ to approximately $q = 8$ Å^{-1}. The experimental setup is similar to an apparatus already described in the literature.[3] The electron spectrometer has no monochromator, but contains a low-work function, indirectly heated oxide cathode operating at about 1000 °K. The Maxwellian distribution of the emitted electrons at this temperature is about 0.25-eV wide and determines the system resolution, since the hemispherical analyzer has a much higher resolution. The current arriving at the sample can be as high as 10^{-6} A. Our measured momentum resolution is $\Delta q \sim 0.15$ Å^{-1}. The large current at the sample allows one to go out to higher momentum transfers where the cross sections are smaller and to utilize thinner samples where multiple-scattering effects may be minimized.

For a simple metal like Be and for momentum transfers $q \leq 1$ Å^{-1}, the excitation spectrum of the valence electrons is dominated by the plasmon around 20 eV which is well separated from the excitation of the K electrons into empty states above the Fermi level with a threshold of about 110 eV (see Fig. 1 for a typical spectrum near $q = 0$). In the neighborhood of the K edge the spectrum compares closely to the optical spectrum obtained using synchrotron radiation.[4] At higher q values the valence-band spectrum moves out to higher energies showing free-electron-like behavior. For

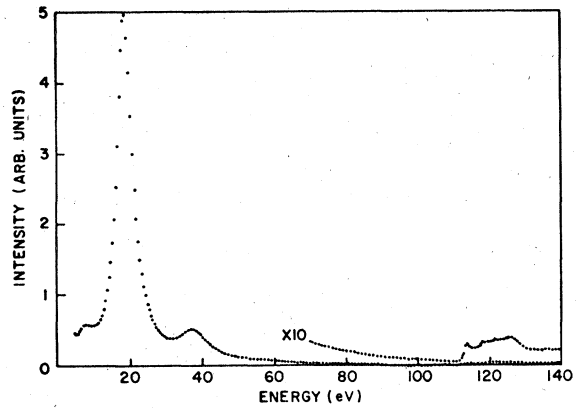

FIG. 1. Total electron energy-loss spectrum at $q = 0$ for Be using 200–225-keV electrons. Units are arbitrarily scaled.

large $q \simeq 6$ Å^{-1}, the K-edge spectrum and the valence-electron spectrum begin to overlap. In this brief note we will not discuss this rather interesting and complicated region of overlap,[5] but focus our attention on the low-momentum ($q \leq 5$ Å^{-1}) region. In fact, we will restrict our attention to spectra with $q \leq 3$ Å^{-1}, where multiple-scattering effects may for these samples and for this energy range be neglected.[6]

We show that the detailed behavior of the spectrum around 100–140 eV is only very roughly described by a one-electron band-structure calculation of Be and that significant deviations exist. The detailed shape, in particular the intensity of the various features, depends on both the density of states and transition matrix element for this system. Our results point out dramatically the fact that simple one-electron pictures, which work well near the Fermi surface are not valid for electron energies some 20 eV above the Fermi surface. The discrepancies must come from the neglect in this one-electron picture of excited-electron-hole, excited-electron, conduction-electron, and hole-conduction-electron interactions.

Although optical data[4] provide us with similar information near $q = 0$, the matrix-element effects associated with finite momentum-transfer scattering gives us information not obtainable by other techniques. The q dependence of the results for the experiment, though not startling at $q \leq 3$ Å^{-1}, suggest that such data will provide stringent tests of more complicated descriptions of the core-excitation process.

The valence and conduction-band structure of Be has been studied in great detail in the past. In the initial application of the orthogonalized-plane-wave (OPW) method, Herring and Hill[7] discussed various electronic properties of Be. Later, a number of more elaborate band-structure calculations on Be appeared using the augmented-plane-wave (APW) method,[8] the OPW method,[9,10] and the nonlocal pseudopotential method.[11] The main purpose of these studies was to explain de Haas–van Alphen Fermi-surface measurements.[12] While significant differences as to the detailed shape of the Fermi surface existed between the various calculations, the overall band-structure features agreed over a 20-eV range measured from the bottom of the conduction band (all energies are measured from this point).[11]

In the present work we have used the nonlocal pseudopotential, defined in Ref. 11 to calculate the valence- and conduction-band structure and associated wave functions of Be up to 40 eV. In the particular form used in Ref. 11, the pseudopotential matrix taken in a plane-wave representation, of the one-electron Hartree-Fock Hamiltonian $H(2m = \hbar = e^2 = 1)$ is

$$H_{ij} = |\vec{k} + \vec{G}_i|^2 \delta_{ij} + S(\vec{G}_i - \vec{G}_j) \times [V_L(|\vec{G}_i - \vec{G}_j|) + V_{NL}(\vec{k}, \vec{G}_i, \vec{G}_j)] . \quad (4)$$

The local form factor $V_L(Q)$ is taken from atomic wave functions. Its Fourier transform evaluated at reciprocal-lattice vectors is arbitrarily cut off at $|G| = 2.6$ a.u. This yields four parameters which are then adjusted to fit the Fermi surface of Be.[11] The nonlocal potenial V_{NL}, operating on s electrons, has the OPW form,

$$V_{NL}(\vec{k}, \vec{G}_i, \vec{G}_j) = [E(\vec{k}) - E_{1s}] \frac{\langle \vec{k} + \vec{G}_j | 1s \rangle \langle 1s | \vec{k} + \vec{G}_i \rangle}{\langle 1s | 1s \rangle} . \quad (5)$$

The orthogonality matrix elements appearing in V_{NL} are calculated using atomic wave functions.[13] While a constant value of $\Delta E = E(\vec{k}) - E_{1s} = 8.64$ Ry was used in Ref. 11 to evaluate Fermi-surface properties, the energy dependence of V_{NL} should be considered for describing the behavior of the excited states over a wide energy range. We have varied ΔE from 8.5 to 11.0 Ry in test calculations. The main effect of such a variation is to modify the overall bandwidth of the spectrum. In this paper, we will use the more convenient form of V_{NL} with a constant average $\Delta E = 9.5$ Ry.

The pseudopotential matrix was diagonalized in a truncated plane-wave basis set using a kinetic energy cutoff of $|G|^2 = 2.5$ Ry corresponding to 11 plane waves at Γ. The wave functions and energies were determined at 225 $\vec{k}$ points in the irreducible part of the hexagonal Brillouin zone. The matrix elements appearing in Eq. (2) were evaluated in an OPW framework, similar to optical matrix elements.[14]

$$\langle \psi_{\vec{k}} | e^{i\vec{q}\cdot\vec{r}} | 1s \rangle = \langle \phi_{\vec{k}} | e^{i\vec{q}\cdot\vec{r}} | 1s \rangle - \langle \phi_{\vec{k}} | 1s \rangle \times \langle 1s | e^{i\vec{q}\cdot\vec{r}} | 1s \rangle , \quad (6)$$

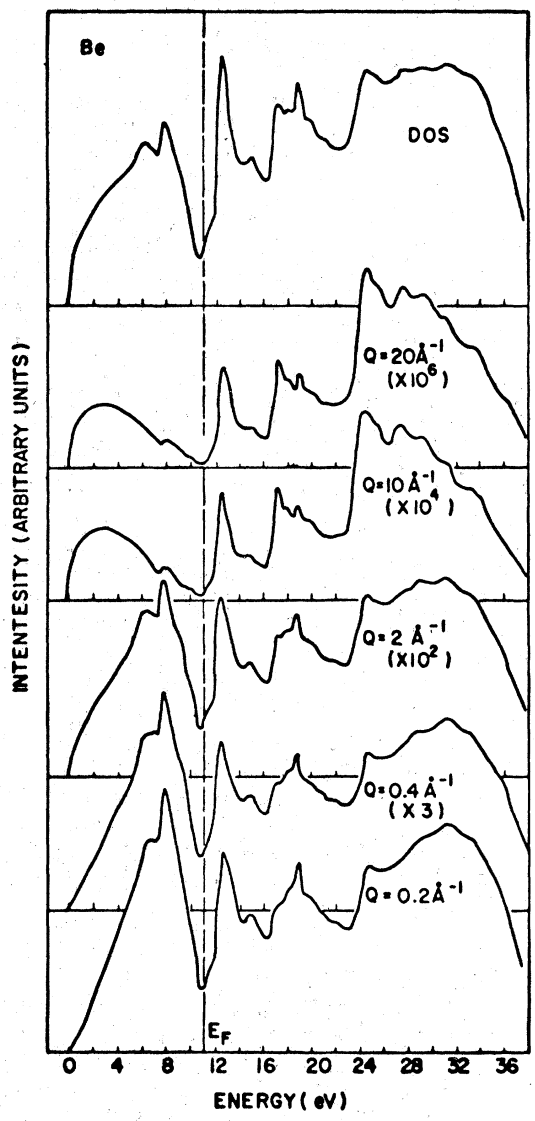

FIG. 2. Theoretical density of states (top) and K-edge electron-loss spectra (bottom) with varying momentum transfer q for Be. The spectra are arbitrarily scaled in amplitude to facilitate comparison.

where $|\psi_{\vec{k}}\rangle = |\phi_{\vec{k}}\rangle - \langle 1s|\phi_{\vec{k}}\rangle |1s\rangle$ is an OPW derived from the pseudo-wave-function $|\phi_{\vec{k}}\rangle$. Given the matrix elements, the sum over the Brillouin zone in Eq. (1) was carried out using the Gilat-Raubenheimer scheme.[15] To compare the theoretical results to experiment, $S(\vec{q}, \omega)$ was directionally averaged.

In Fig. 2 theoretical results are presented for $S(\vec{q}, \omega)$ for q values ranging from 0.2 Å^{-1} up to 20 Å^{-1}. The amplitudes have been scaled arbitrarily to bring the spectra on a comparable scale. Also indicated for comparison is a bare density of states (DOS). It shows that the main structures in $S(\vec{q}, \omega)$ originate from DOS features rather than from matrix elements. Most striking is the deviation of the density of states from its free-electron parabola for energies larger than about 8 eV relative to the bottom of the conduction band. This feature, which has been noted earlier,[7] is due to the strong crystalline potential which p electrons experience due to the absence of any core orthogonality repulsion. In fact, the DOS starts off free-electron-like for the s-like states at the bottom of the valence band, but begins to vary strongly as band-structure effects appear and mix in p states with the first Bragg reflection around 11 eV.

Several interesting overall changes occur in $S(\vec{q}, \omega)$ as q increases. For small q values the transitions are dipolelike and selection rules favor the p-like part of the valence-band spectrum. Thus the spectrum below the Fermi surface is quite distorted from the pure DOS curve (see Fig. 2). As q increases, notably above 2 Å^{-1}, the s-like part at the bottom of the band becomes drastically enhanced at the expense of the p-like peak around 8 eV. It should, of course, be noted that these states are occupied, and thus inaccessible to our experiment. Above the Fermi level several changes occur, though of minor strength. The fact that the major changes in the theoretical spectrum occur for momentum transfer $q \approx 10$ Å^{-1} is easily understood. As we see from Eq. (6) the matrix elements are expected to show structure only when $1/q$ becomes comparable in size to the $1s$ core radius, in this case ≈0.1 Å, of Be. Accordingly, valence-electron spectra should show a significantly stronger q dependence due to the increased spatial extension of these states.

In Fig. 3 theory and experiment are compared for $q = 0$ and $q = 3$ Å^{-1}. The spectra are brought to a common energy scale by aligning the predominant peak at about 114 eV. The $q = 3$ experimental data have been corrected for a 6% multiple-scattering effect. These 400-Å samples are highly transmitting (≈70%). The main multiple-scattering event is an elastic event followed by a forward (or near-forward) inelastic scattering. By using the measured ratio of the transmitted beam to the inelastically scattered beam in the forward direction one can determine the amount of $q = 0$ spectrum to be subtracted from the data. This small subtraction makes very little difference between the data in Fig. 3(b) and the raw data. In addition, in each data set a flat multiple inelastic background has been subtracted. The theoretical curve, of course, has an arbitrary normalization. It is normalized so that the two curves are offset from one another. Only the relative strengths of any of the features have meaning.

There exists considerable discrepancy between

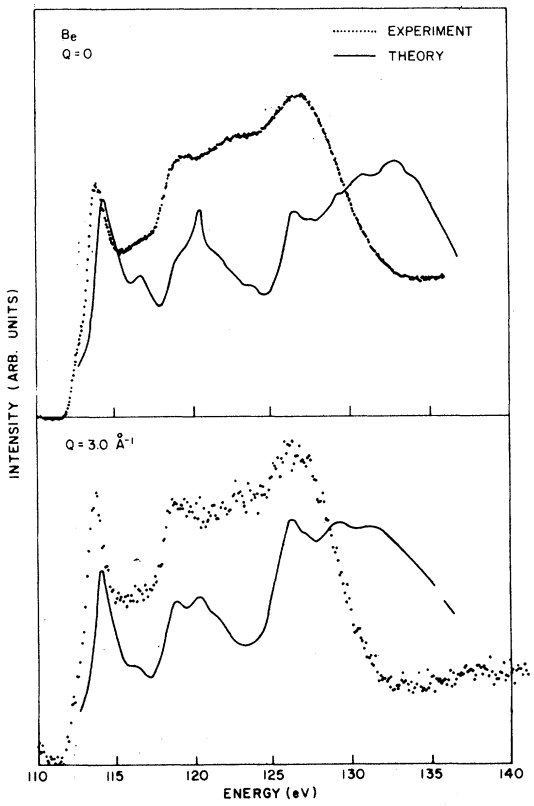

FIG. 3. Comparison between measured (dots) and calculated (solid line) K-edge electron energy-loss spectra for $q=0$ and $q=3$ Å^{-1} momentum transfer. Units are arbitrarily scaled.

theory and experiment. The shape of the main peak at 114 eV near the Fermi surface fits quite well. Furthermore, structures in the theoretical spectra ranging from 125 to 135 eV seem to fit well with experiment, even insofar as the q dependence is concerned, provided they are shifted down in energy by about −5 eV. The excessive bandwidth of the theoretical spectra is probably due to the use of an energy-independent repulsive pseudopotential. In fact, the only other theoretical DOS result, a curve presented in Ref. 4 which is based on OPW calculations of Ref. 9, shows a somewhat smaller bandwidth but similar strong peak structures, not observed in experiment. This general trend, that the theoretical one-electron calculations show considerably more structure, is not a matter of experimental resolution, since the strong peak close to the Fermi level at 114 eV is well reproduced. While certainly more detailed and realistic one-electron calculations are necessary for a quantitative analysis, several of the aforementioned discrepancies may be indicative of the existence of higher-order electron-electron interaction effects in the experiment. In fact, for energies some 10–20 eV above the Fermi level and for momentum transfers as discussed here, the excited electrons may undergo various loss processes which, due to the absence of strict selection rules, would tend to wash out sharp structures present in the one-electron spectra.

In conclusion we have measured the K-edge spectrum in Be with electron-energy loss of variable momentum transfer. The measurements are compared to theoretical calculations using an energy-independent pseudopotential. While several key features in the spectra can be well identified, significant discrepancies between theory and experiment remain. Some of these discrepancies can certainly be removed by performing more accurate one-electron calculations. It is, however, argued that many-electron excitations which are present in the experiment are likely to wash out sharp structures in the one-electron spectra and thus are mainly responsible for the discrepancies.

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