tion data in $SrTiO_3$, giving $\eta \sim 1.1 \pm 0.1$ for $\epsilon < \epsilon_\Delta$ and $\eta \sim 2.2 \pm 0.2$ for $\epsilon > \epsilon_\Delta$.

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Band-Structure Contributions to X-Ray Emission and Absorption Spectra and Edges in Magnesium*

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The soft-x-ray $L_{2,3}$ emission and absorption spectra of Mg metal have been determined by means of high-resolution *ab initio* augmented-plane-wave calculations. The inclusion of transition-matrix elements calculated from the augmented-plane-wave wave functions changes the sharp structure found in the joint density of states, yields an $L_{2,3}$ emission spectrum in good agreement with experiment, and indicates that band-structure effects play an important role in the observed x-ray threshold shape.

Despite both intensive and extensive efforts, the theoretical understanding of x-ray emission and absorption edges in metals is still a subject of controversy and disagreement mainly because of the differing roles assigned to band-structure (one-electron) and conduction-electron–core-hole, final-state interaction (many-body) effects.[1,2] In the simple metals Li, Be, Na, Mg, and Al the shapes of the observed threshold edges in both emission and absorption fail to exhibit the sharp step-function edges expected to be characteristic of free-electron metals. Instead, experimentally determined edges are either sharp and peaked at threshold (e.g., the $L_{2,3}$ edges of Na, Mg, and Al) or broad and rounded (e.g., the K edges of Li, Be, Mg, and Al) over energies ≈ 1 eV. Since these features and especially the sharply peaked nature of the $L_{2,3}$ edges do not seem explicable in a one-electron theory based on the free-electron model, many-body models were developed by Mahan[3] and Nozières and de Dominicis[4] in which the conduction-electron–core-hole interactions play a central role. These theories predict threshold edges whose shapes are characterized by threshold exponents α_0 (for $L_{2,3}$ edges) and α_1 (for K edges); for photoemission the asymmetry

of the line shape is characterized by[5] $\Delta \equiv -\alpha_\infty$. Serious objections have, however, been raised recently about the results of the many-body theory since the accepted values of the parameters in the theory produce threshold shapes that are either inconsistent with or different from the experimental data. Indeed, Slusky *et al.*[6] have found that they cannot consistently describe their electron-energy-loss experiments on Mg assuming that the line shapes are caused exclusively by the Mahan–Nozières–de Dominicis effect.

It has been widely believed that the simple metals mentioned above are largely free-electron like. Yet Fermi-surface–related experimental data also indicate that deviations from sphericity in their Fermi surfaces exist, especially in polyvalent metals. In order to access the importance of these generally ignored one-electron effects, we have undertaken a study of the $L_{2,3}$ emission and absorption spectra of Mg metal based on the calculation of the Bloch energies and Bloch functions determined by the augmented-plane-wave (APW) method. To assure an accurate calculation of both the density of states and the x-ray intensities, energy eigenvalues and wave functions were calculated at 495 nonequivalent points in the irreducible $\frac{1}{24}$th portion of the first Brillouin zone. We find that, despite the nearly parabolic nature of the bands, both the density of states and the x-ray intensities show sharp structures, including peaks at, below, and above the Fermi energy, E_F. These rather dramatic results indicate that the one-electron or the band-structure effects may be important for understanding edge effects in simple metals.

The x-ray emission or absorption intensity $I(E)$ in the one-electron approximation is given by

$$I(E) = C\int d^3k\,|\langle\psi_c|\nabla|\psi_k\rangle|^2\delta(E-E_k+E_c)$$
$$= C\sum_k \int \frac{dS_k}{|\nabla_k E_k|}|\langle\psi_c|\nabla|\psi_k\rangle|^2. \quad (1)$$

Here ψ_k and E_k are, respectively, the Bloch function and the Bloch energy of an electron in the conduction band with wave vector $\vec{k}$ and band index n (k includes both $\vec{k}$ and n), ψ_c is the core function ($2p$ function for the Mg $L_{2,3}$ spectrum) with energy E_c, and C is simply a constant of proportionality. The integral in (1) is over constant-energy surfaces, $E = E_k - E_c$, where the conduction-electron energies E_k are restricted to the occupied states for emission and to the unoccupied states above the Fermi energy for absorption.

It is clear from Eq. (1) that if the transition-matrix elements (TME) $\langle\psi_c|\nabla|\psi_k\rangle$ are taken constant, then the x-ray intensities are proportional to the density of states (DOS). In the case of the completely free-electron metals this assumption would lead to the parabolic $[\propto (E-E_c)^{1/2}]$ shape of the emission spectrum. We note, of course, that the free-electron approximation is not correct in that, because of the dipole selection rules, only the partial densities of states (s and d for $L_{2,3}$ spectra) contribute even in the constant-TME approximation. To locate any possible structure in the DOS and in the x-ray spectrum it is important that Eq. (1) be evaluated as accurately as is possible. The standard histogram or the sampling method, for instance, is unreliable for this purpose; instead we have used the tetrahedron method[7] which has been found to be a simple and highly accurate scheme for Brillouin-zone integrations.

The energy-band calculation was performed using the warped muffin-tin version of the APW method; i.e., the potential was not assumed to be constant within the interstitial region. The potential was derived from the superposition of the atomic charge densities calculated from the self-consistent Hartree-Fock-Slater program of Herman and Skillman with an assumed $3s^2$ atomic configuration and the Slater exchange parameter $\alpha = 1$. With a fixed basis set of 32 reciprocal-lattice vectors chosen for the expansion of the wave functions, the eigenvalues were iterated until they converged to within 1 mRy. The resulting energy bands and Fermi surface are found to agree well with previous calculations.[8]

Figure 1 presents our density-of-states results. We first note that the DOS is remarkably parabolic over the bottom three-fourths of the occupied part of the band but that as one proceeds to higher energies some large peaks appear (which can be related to the flatness of the bands in some parts of the Brillouin zone), including an important peak in the DOS at the Fermi energy itself. Since we are concerned with transitions involving a $2p$ core state we have included in Fig. 1 a decomposition of the DOS into partial densities of states of s, p, and d character. Whereas the s DOS dominates well below E_F, the p and d contributions increase with increasing energy, resulting in a large p DOS at E_F; surprisingly, the d contribution at E_F is also large in that it is about one-half of the s contribution.

The TME's which enter Eq. (1) were found to

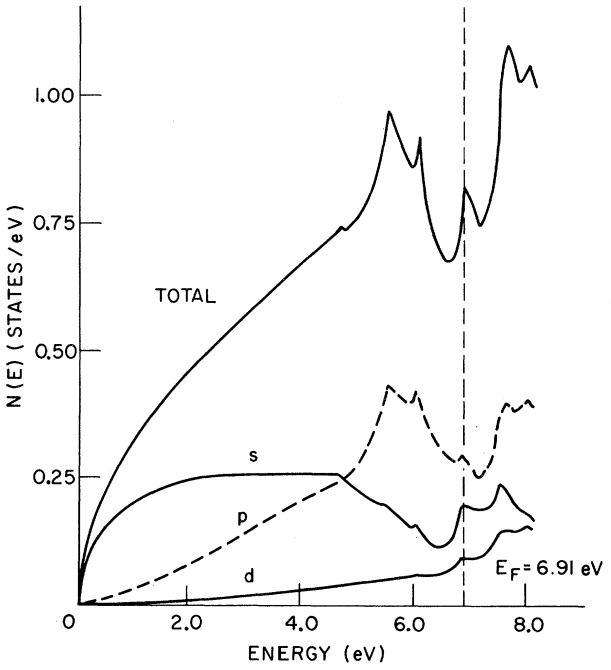

FIG. 1. APW density of states for Mg metal; the partial densities of states include contributions from muffin-tin spheres only.

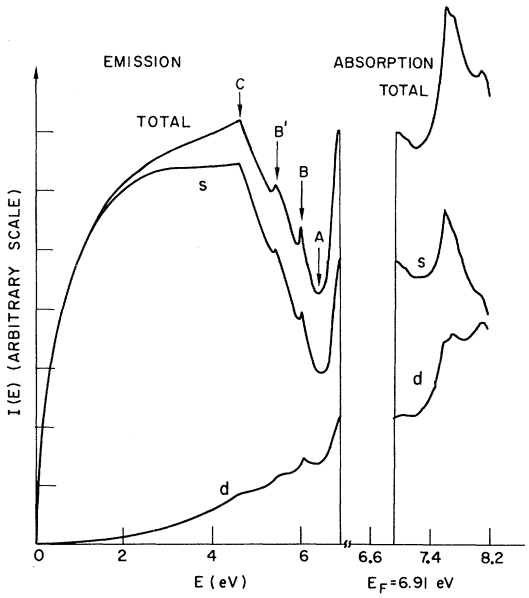

FIG. 2. X-ray emission and absorption (on an expanded scale) spectra for Mg metal.

show significant variations throughout the zone, indicating that the constant-TME approximation is not appropriate. We have used Eq. (1) and the TME values calculated using the APW wave functions for all the 495 inequivalent points in the irreducible $\frac{1}{24}$th Brillouin zone to determine both an $L_{2,3}$ emission and absorption spectrum based solely on the band model. The results, presented in Fig. 2 in arbitrary units for $I(E)$ (and with an *enlarged* energy scale for the absorption curve to emphasize its features), show that essentially all the features found in the partial DOS (of Fig. 1) are present, but enhanced, in the x-ray spectra. As before, we show the separate l contributions to the total intensity curves. The d contribution is seen to be small in the parabolic region of the emission spectrum but increases at higher energies and contributes about 30% to the spectrum at E_F. Perhaps the most important feature of our calculated emission curve, to be discussed later, is the sharp peak at the Fermi energy. The sharp structure in the s contribution results in structures labeled A, B, and C which correspond very well to the structure in the $L_{2,3}$ emission spectrum observed by Watson, Diamond, and Fabian.[9] (These authors report that these discontinuities were observed consistently in measurements performed in two different laboratories.)

The discontinuity marked B' in our spectrum has not been reported experimentally; it may be too small to be seen experimentally when a broadening function is added to the "raw" calculations shown in Fig. 2.

The raw absorption spectrum, also shown in Fig. 2, was determined by a similar procedure. Here we note that there is a weak peak close to E_F and a strong peak at 7.56 eV (or 0.65 eV from E_F) which arises from structure in both the s and d contributions. Comparison of these results with the DOS results of Fig. 1 indicates that the effect of the TME's has been to enhance somewhat the s contribution. The most prominent features of our calculated spectra are the peaks at the Fermi energy, which look strikingly similar to the observed absorption- and emission-edge anomalies. Hence one-electron effects contribute significantly to the observed edge shapes; and threshold exponents α_0 extracted from data assuming a Nozières–de Dominicis many-body enhancement of energy-independent one-electron spectra are likely to be significantly larger than the true threshold exponents—making the many-body effects in the spin independent Nozières–de Dominicis theory smaller than previously believed. We are unaware of any published analyses of Mg $L_{2,3}$ edge data which account for extensions of the Nozières–de Dominicis theory to include spin-dependent scattering[10] or exchange mixing[11] of L_2 and L_3 edges, as recently proposed by Gir-

vin and Hopfield[10] and by Onodera[11]; conceivably these effects could also influence the $L_{2,3}$ edge shape, as could phonon and lifetime broadening. We have not analyzed the $L_{2,3}$ edge data for Mg in an effort to separate one-electron and many-electron effects because we feel such analyses may be misleading. The calculated spectra certainly exhibit spikes at the $L_{2,3}$ edges but the precision may be insufficient to permit confident extraction of accurate many-body exponents from spectra whose many-body enhancements are small to begin with. Thus we conclude that (1) one-electron band-structure effects are significant in Mg and may be significant at x-ray thresholds in other free-electron metals as well, and (2) the $L_{2,3}$ edge of Mg is a poor testing ground for many-body threshold effects.

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Electronic Structure of Amorphous Semiconductors*

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The Fermi energy as a function of electronic density and temperature is calculated for a defect level in which the effective intrasite electronic correlation energy is negative. It is found that the Fermi level lies *below* the energy of the highest-filled quasiparticle state, even at $T=0$, a result which favors p-type conduction. Futhermore, the Fermi energy varies only very slowly with electronic density and temperature, and thus is effectively pinned.

Although amorphous semiconductors exhibit as wide a range of electronic behavior as crystalline semiconductors,[1-3] they can be subdivided into two major classes with sharply different properties. Amorphous solids made up primarily from Group-IV or Group-V elements typically have n-type thermopower,[4] exhibit variable-range hopping at low temperature,[5] show an EPR signal,[6] and have a Fermi energy which can be moved by varying the electronic density.[7] In contrast to this, chalcogenide glasses generally have p-type thermopower,[4] do not exhibit variable-range hopping,[1-3] do not show an EPR signal,[8] and have a Fermi energy which does not vary much with electronic density.[9] In order to explain some of these properties, Street and Mott[10] proposed a model in which the localized states in the gap of chalcogenide glasses appear at dan-