

ic excitation spectra of all ferrites with only two adjustable parameters Δ_B and ΔE , since the linewidth Δm and k , which may be different in the various ferrites which range from metals to insulators, does not enter the ESP data critically.

This is one of the few cases in which a simple model explains data obtained by photoemission in a quantitative way.

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$L_{2,3}$ Transitions in Liquid Na and Al: Edge Singularity and Extended X-Ray-Absorption Fine Structure

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The $L_{2,3}$ excitation spectra of liquid and solid Na and Al were measured at several temperatures throughout the energy intervals 30–80 and 70–170 eV, respectively, using yield spectroscopy. The spike at the 31-eV Na edge is virtually unchanged in the liquid, indicating that the edge is insensitive to long-ranged crystalline order. The broader structures up to 100 eV above the edges in Na and Al, however, are washed out in the liquid.

Recently considerable theoretical effort has been devoted to the interpretation of the photoabsorption spectra of electrons initially orbiting in the $2p$ core levels of simple metals; one-electron theories offer competing explanations of structures both at the $L_{2,3}$ thresholds and as much as 100 eV above.

At the $L_{2,3}$ edges, the threshold spikes seemed to be well explained by the many-body theory of Mahan¹ and Nozières and De Dominicis,² which attributed the observed spikes to the shielding of the core hole by conduction electrons. However, the same theory also predicted the rounding of K edges and contained a parity selection rule which led to predictions of conspicuous dependence of edge shapes upon momentum transfer³ in x-ray Raman scattering or electron energy-loss scattering. Dow and co-workers⁴ have disagreed with the many-body explanation of the Li K -edge rounding and have proposed a phonon

core-level broadening mechanism to explain the edge shape. We have recently observed thermal broadening in the region of the absorption threshold.^{5,6} Tests of the many-body theory's selection rule by Sonntag⁷ (in $\text{Li}_{1-x}\text{Cu}_x$ alloys) and by Ritsko, Schnatterly, and Gibbons⁸ (using electron energy loss) did not produce the predicted changes of the Li edge shape. From these and other facts,⁹ questions arise concerning the limitation of the many-body theory. Nevertheless the spike at the Na $L_{2,3}$ edge still provides an outstanding experimental support of this theory. Unlike similar, though weaker, features at the $L_{2,3}$ edges of Mg and Al the spike in Na cannot be easily dismissed as a density-of-states structure. Its behavior upon melting should provide valuable clues to its origin and to its dependence on long-ranged crystalline order.

The spectral region well above the $L_{2,3}$ edges is the subject of yet another theoretical dispute

concerning the relative importance of plasmarons (localized plasma oscillations)^{10, 11} and extended x-ray absorption fine structure (EXAFS).^{12, 13} The first plasmaron calculation yielded a spectrum in good agreement with the observations for Al, featuring the prominent peak at 24 eV and two shoulders at 15 and 30 eV above the $L_{2,3}$ threshold. Moreover similar structures appear in the $L_{2,3}$ spectra of solid Na and Mg, but are absent from the gas-phase spectra of Na¹⁴ and Al,¹⁵ a fact consistent with either a collective plasmaron model or an EXAFS long-ranged order model, but inconsistent with an atomic model. However, the structures in the solid-state data for Na and Mg did not exhibit the plasmaron theory's scaling with free electron density. Recently Ritsko, Schnatterly, and Gibbons¹⁶ have reinterpreted these structures as EXAFS, that is, as interference of the outgoing electron wave as it is coherently backscattered by neighboring atoms, causing the electron's amplitude at the hole to be an undulating function of its energy. The EXAFS effect is sensitive to the details of crystalline order, whereas the plasmaron effect depends only on the mean electron density; hence if melting washes out the disputed structures, the EXAFS model should be judged superior to the plasmaron model.

The results were obtained using monochromatized¹⁷ synchrotron radiation from DESY as a source (resolution ~ 0.10 at 50 eV photon energy) and detection of the partial photoelectric yield using a low-resolution (~ 1 eV) electron energy analyzer¹⁸ to separate scattered and thermally emitted electrons. The partial photoyield is known to be proportional to the absorption coefficient.¹⁹ The samples were cleaned and maintained in a vacuum of approximately 10^{-10} Torr; care was taken to keep the initial oxide layer on the Na samples thin and to remove it after melting by scraping and stirring the samples with a tungsten wire brush. Clean Na, once obtained, could be maintained without indications of oxidation as a liquid for many hours and as a solid for approximately one hour. The temperatures of the Na samples were measured with a thermocouple and ranged from liquid nitrogen temperature (LNT) to 390 K (the melting point is 371 K).

Al had to be supported on Al_2O_3 ceramics because of its tendency to alloy with all metals; and the ceramics, being insulating, would become charged at lower temperatures, restricting the measurements to the range 500 to 1000 K (the melting point is 933 K). The temperature of the

Al sample was not measured since we were not able to apply a protected thermocouple in good thermal contact with the sample.

Since the ratio of photoyield and absorption coefficient is known to be a slowly varying function of photon energy,¹⁹ we determined this function from measured LNT absorption²⁰ and yield data for Na. This empirical ratio was then used to calculate absorption coefficients from yield data, permitting determination of the otherwise inaccessible liquid absorption coefficients. For Al a similar procedure was applied.

The results for Na are displayed in Fig. 1; the relative scales for solid and liquid Na are arbitrary. If the curves are normalized to bring them into coincidence near the $L_{2,3}$ threshold, the general shape of the threshold spike is unchanged. (The experimental accuracy is approximately 10% below 35 eV—low photon intensity—and approximately 3% elsewhere.) The threshold broadens perceptibly upon melting, and the spin-orbit splitting is barely discernible in the liquid photoyield although easily resolved in absorption measurements at LNT.²¹ The reduced accuracy of the partial yield measurement precludes a quantitative analysis of changes in spike shape. However, the fact that the spike survives the solid-liquid transition practically unchanged excludes any explanation of the effect as generated by long-ranged crystalline order. The data are consistent with an interpretation which involves the core hole in contact with a free electron gas as given by the presently available many-body theo-

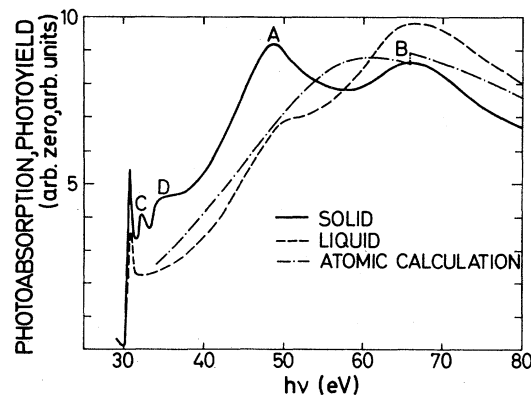


FIG. 1. Photoabsorption (Refs. 20 and 21) and photoyield of solid and liquid Na in the region of $L_{2,3}$ absorption. Absorption and yield of solid Na was obtained at LNT (same curve, see text). The liquid (yield) was measured at 390 K. Included are results of an atomic calculation by McGuire (Ref. 22).

ries¹ or with an effect generated by short-ranged order or depending only on the mean density of the conduction electron gas.

We now examine the spectra above the edges, where there are striking differences between the solid and the liquid spectra. For Na, the structures *A* and *B* are washed out in the liquid leaving a shape similar to the spectrum of Na vapor¹⁴ and the free-atom spectrum calculated by McGuire.²² When samples are warmed from liquid nitrogen to room temperature, the region between *A* and *B* changes continuously, with the minimum filling in and flattening out. The structures *C* and *D* are also absent from the spectrum of liquid Na and might be associated with peaks in the solid's density of states or possibly with traces of oxide. The spectra of Al (Fig. 2) exhibit the same washout of structure observed for Na. Indeed in the solid these structures seem to sharpen continuously with decreasing temperature: Shortly after solidification the structures are very weak, and after one hour of cooling they are sharper but less pronounced than in room-temperature spectra.²⁰

The dependence of the Na and Al spectra on temperature and on phase change are inconsistent with the plasmaron theory and demonstrate the importance of long-ranged order in shaping these structures. Hence these data are consistent with an EXAFS model, in which the radial distribution function determines the positions of the peaks. In the solid phase, the radial distribution function has well-defined peaks associated

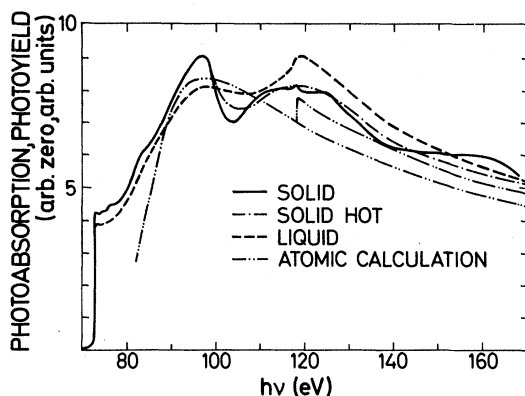


FIG. 2. Photoabsorption (Ref. 20) and photoyield of solid and liquid Al in the region of $L_{2,3}$ absorption. Absorption of solid Al was obtained at RT and yield at about 500 K ("solid hot"). The liquid (yield) was measured at about 1000 K. Included are results of an atomic calculation by McGuire (Ref. 22).

with crystalline order, which blur with increasing temperature. In the liquid phase only the nearest-neighbor peak in the radial distribution function remains prominent, and the EXAFS structure is blurred.

Using square well potentials and a method similar to that of Ritsko, Schnatterly, and Gibbons¹⁶ we have attempted a simple model calculation of the EXAFS structure for the interpretation of preliminary results on Al,¹⁸ and were able to reproduce qualitatively the blurring of structure. However, Ashley and Doniach¹³ have shown that EXAFS in this low electron-kinetic-energy regime is dominated by multiple scattering of the electron by first and second nearest neighbors. Thus a quantitative analysis of these data will require a more sophisticated EXAFS theory, possibly including initial and final state symmetry²³ or a method of matching atomic and solid state wave functions, as proposed by Fano.²⁴

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Self-Consistent Pseudopotential Calculation for a Metal-Semiconductor Interface*

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The electronic structure of a jellium-Si interface is calculated with use of a jellium density corresponding to Al and self-consistent Si pseudopotentials. Local densities of states and charge densities are used to study states near the interface. The states which exist in the Si fundamental gap are bulklike in jellium and decay into Si with high concentration in the dangling-bond free-surface-like Si state. The calculated barrier height is in excellent agreement with experiment.

In this Letter we present the first self-consistent pseudopotential calculation for the electronic structure of a metal-semiconductor interface. The calculation models an Al-Si interface with a jellium potential representing the aluminum-ion potential in contact with the Si (111) surface. The calculated barrier height is in excellent agreement with recent experimental results.¹ Various states which exist near the interface are identified and discussed. In addition to displaying the total valence charge density and the charge density of a localized interface state, we present a local-density-of-states (LDOS) calculation. The LDOS, which displays the density of states in real space, facilitates the identification and illustrates the characteristics of the various kinds of states at the interface.

Metal-semiconductor interfaces have been subjected to many discussions and speculations²⁻⁹ as a result of their great importance in device application. However, regrettably, past theoretical investigations into their electronic structure have been mostly qualitative or semiquantitative. Experimentally, for covalent semiconductors such as Si, the interface barrier height

is found to be essentially independent of the metal contact and of the doping in the semiconductor.^{1, 10, 11} Bardeen² attributed this behavior to a high density of surface states in the semiconductor gap; that is, the Fermi level is pinned by the surface states. Heine,³ on the other hand, pointed out that semiconductor surface states cannot exist in the semiconductor gap if this energy range is inside the metallic band. He suggested that the pinning of the Fermi level is due to states of a different type in the semiconductor gap. These states are composed of the states from the tails of the metallic wave functions decaying into the semiconductor side. Recently Inkson,^{4, 6} using a model-dielectric-function formulation, proposed that the pinning of the Fermi level arises from the narrowing of the semiconductor gap at the interface. According to Inkson, the screenings for the valence band and for the conduction band are different near the interface. This causes the valence band to bend up and the conduction band to bend down and eventually the bands merge together at the interface for a covalent semiconductor.

Our calculations give results which are closer