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Solid-state effects in photoionization cross sections of d states: Comparison between MoS_2 and Mo

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The photoionization cross section σ of $4d_{z^2}$ states of Mo in $2H$-MoS_2 in the photon energy range 65–200 eV is compared with the $4d$ cross section from the bonding states of bcc Mo and with theoretical values for isolated Mo atoms. The $h\nu$ dependence of σ in MoS_2 is very close to the atomic σ with some deviations at higher $h\nu$, whereas the σ from Mo metal is severely distorted. An interpretation scheme is suggested to connect these differences in the cross sections to the different arrangements of the electron states in the solids.

We have shown recently that changes in the photoionization cross sections (σ) of $4d$ and $5d$ states on passing from isolated atoms to the solid can be qualitatively discussed in terms of the degree of atomiclike behavior of the d orbitals in the solid.[1–3] This is particularly significant in connection with the modification of the so-called Cooper minimum, which is well known at the atomic level and which basically originates from a cancellation in the dipole matrix element.[4,5]

The crucial problem now is to clarify to what extent the modifications of the $\sigma(h\nu)$ with respect to the atomiclike behavior can be related to the non-atomic-like behavior of the electron states in the solid, i.e., to what extent photoelectron cross sections can be used as a new probe of the chemical bond in solids. This can be of paramount importance in consideration of the relative simplicity of the measurements of $\sigma(h\nu)$ and of the increasing availability of synchrotron radiation.

The present work adds important new information to our previous papers[1,2] and contributes to the understanding of this solid-state effect. The work is based on a comparison of the experimental σ of the same atomic orbitals in different solid structures, showing how the differences on the wave functions are reflected in the cross sections. We compare the σ in the range 65–200 eV for Mo $4d$ states in a case of marked distortion[1] with respect to free atoms (bcc Mo) and in a case ($2H$-MoS_2) which is a good candidate for an atomiclike behavior.[6] We give here the first experimental σ_{4d} in MoS_2 measured for this purpose with the same method and apparatus used for Mo (Ref. 1), we compare the experimental results with theoretical σ for atomic Mo (Ref. 7), and we suggest an interpretation scheme.

Experimental details of the present work performed at Stanford Synchrotron Radiation Laboratory (SSRL) were presented in our previous work[2] and are not repeated here. It suffices to say here that the light was at near-normal incidence to the sample so that reflectivity corrections were negligible. The spectra were recorded with a double-pass cylindrical mirror analyzer (CMA), with the analyzer axis at right angles to the light (and so the measurements were integrated over a large solid angle). The MoS_2 sample was natural $2H$-MoS_2 crystal, characterized with x rays, and cleaved *in situ* (base pressure 5×10^{-11} Torr). Since a MoS_2 single crystal was used, diffractive effects are also present in the measurement. Fortunately, these effects take place at energies different from that of the Cooper minimum, and are easily detected in the σ measured from S $3s$ core states, which must be monotonic in this energy range as shown by atomic calculations;[7] thus, the correction for diffraction effects is obtained easily by considering as a function of electron kinetic energy the ratio ($\sigma_{\text{expt}}/\sigma_{\text{theo}}$) for S $3s$, and does not interfere with the physics discussed here.[8] It is to be remembered that σ values are measured only to within a multiplicative factor, so that the results are relative and not absolute. This is reflected in the discussion which will be carried out at a level which does not require the knowledge of absolute σ values. Needless to say, future experiments giving absolute values will be very useful.

Spectra of the MoS_2 valence band at selected $h\nu$ are shown in Fig. 1 (the results are in agreement with the previous works[6,9] and extend the $h\nu$ range of the available measurements). The valence peaks have S $3p$ and Mo $4d$ atomic origin. It is known[9] that the shallowest peak contains Mo $4d$ states having d_{z^2} nature with very little interaction with S p orbitals; this has been recently confirmed by x-ray emission[10] and x-ray adsorption.[11] MoS_2 has a layered structure, with widely separated strata of atoms. In $2H$-MoS_2 each layer consists of a central Mo hexagonal plane and two nearby S hexagonal arrays;[9,10,12] each Mo atom is at the center of an equilateral prism of S atoms, and the d_{z^2} orbitals have the lobes oriented along the axis of the prism.

The photoionization cross section of $4d_{z^2}$ states is shown in Fig. 2 (lower panel), with the solid line interpolating the experimental points. These results are corrected for photoelectron diffraction; to show that the diffraction correction is not critical we give also the uncorrected experimental cross section (dotted line). The behavior of the two curves

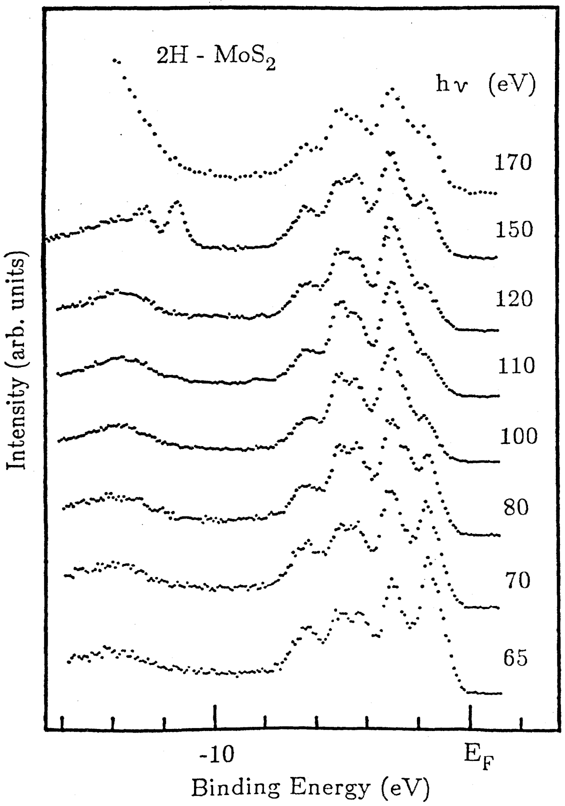

FIG. 1. Angle-integrated photoemission spectra of $2H_1$-MoS$_2$ at various photon energies in the interval 65–200 eV.

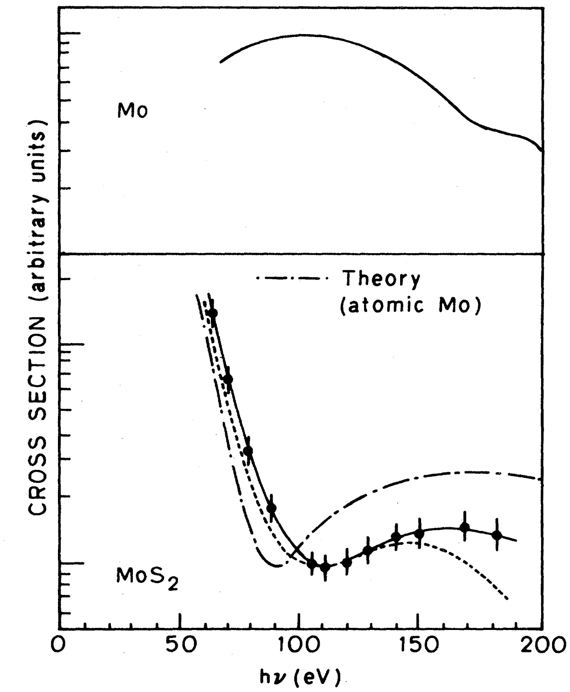

FIG. 2. Logarithmic plot in arbitrary units of photoionization cross sections σ. Lower panel: experimental σ for Mo $4d_{z^2}$ orbitals in $2H$-MoS$_2$ corrected for diffractive effects (solid line) and uncorrected (dotted line), theoretical σ for isolated Mo atoms (dot-dashed line). Upper panel: measured σ for polycrystalline bcc Mo. The error bars give the statistical errors; the measured σ could have systematic distortions due to inaccuracies of photon flux evaluations; this could originate slowly varying distortions (±10%) over the whole $h\nu$ range. The theoretical σ includes a small $h\nu$ dependence due to the asymmetry parameter in the geometry of the experiment.

is very similar and the correction is of importance only at very high $h\nu$. The experimental σ are obtained from the area of the spectra in the interval between the upper edge and -1.2 eV; the choice of this energy is not critical and σ is independent of this value up to $\cong 1.3$ eV within the range of experimental error. At large energies the difficulties due to the S p background make the evaluation of σ uncertain. With this procedure the measured σ pertains exclusively to Mo $4d$ states.

The comparison between the measured σ and the theoretical value is done exclusively by considering the shape of the curves for the reasons given above; a convenient way is to normalize the curves to the same value at the Cooper minimum. This is done in the lower panel of Fig. 2 for the measured σ in MoS$_2$ and for the theoretical σ for isolated Mo atoms (dashed line) calculated in the HFS dipole approximation.[7] In the upper panel we give the σ from the bonding states (between -5 eV and the Fermi level) in polycrystalline bcc Mo measured under strictly comparable conditions, taken from Ref. 1. The difference between the $4d$ cross sections in Mo and in MoS$_2$ is dramatic and the atomiclike behavior in MoS$_2$ is very clear.

We will discuss qualitatively the shapes of the σ given in Fig. 2 by using the fact that the σ at higher $h\nu$ is more sensitive to the initial wave function at low distances and vice versa. This is a known general fact in the dipole approximation[13] and is connected with the oscillatory behavior of the outgoing final-state wave. This feature becomes a kind of "reciprocal space" behavior between $h\nu$ and the r axis when the final state is approximated with a free-electron wave function, since σ becomes proportional to the square of the Fourier transform of the radial wave function of the initial state.[9] In the spirit of an heuristic approach we will use this last approximation to evaluate roughly the distances at which the initial-state information is more relevant in the cross section measured as a function of $h\nu$.

We will consider the ratio of the cross sections measured at two photon energies, which is independent of the fact that σ is measured within a multiplicative factor; thus, this ratio can be immediately compared with the theoretical value. The ratio between the measured σ at the Cooper minimum and at $h\nu = 65$ eV in MoS$_2$ has a clear counterpart in the atomic calculations, apart from a small shift in the $h\nu$ scale. This close correspondence should imply that the initial $4d$ wave function in MoS$_2$ is essentially atomic in the distance region between roughly 1 and 1.6 Å. This is the case since Mo $4d_{z^2}$ orbitals have the majority of the charge along the axis[12] of the S prism with a small lateral ring of charge distorted by the interaction with S within the prism. The z lobes are essentially atomic, as can be understood by considering the atomic positions. The distance between Mo and S planes is 1.55 Å, and the radii of the augmented plane wave (APW) spheres of Mo and S are 1.3 and 1.12 Å, respectively.[12] Thus, in the z direction the main $4d_{z^2}$ lobe can extend up to $\cong(1.55+1.12)=2.67$ Å without interacting appreciably with an adjacent triple layer, which is in any case far away (Mo-S distance in z direction $=4.65$ Å). At $\cong 2.67$ Å the free-atom d density of charge from Hermann and Skillman calculations[14] is reduced by about a factor of $\cong 80$ with respect to the maximum. Thus, the main lobes are not distorted appreciably by solid-state effects at large distances, and this is reflected in a typical atomiclike behavior of the σ at smaller $h\nu$, as shown in Fig. 2. The small shift of the MoS_2 Cooper minimum cannot be discussed at the present in the absence of theoretical investigations; we speculate that it could be due to a small compression of the $4d_{z^2}$ orbitals in the solid. The behavior of σ in MoS_2 beyond the Cooper minimum is still atomiclike, but with greater deviation with respect to the free atom, as expected from the above-mentioned increasing deformation of the ψ at short distances. This qualitative argument appears to be reasonable if one considers that at energies greater than 150 eV the wavelength for a free electron is smaller than $\cong 1$ Å, and that the distance between Mo and S planes is 1.55 Å.

The ratio of the measured cross sections in (bcc) Mo at $h\nu=200$ and 65 is much higher than in MoS_2 and in atomic Mo; this suggests a severe distortion of the initial state in (bcc) Mo with respect to the free atom roughly in the distance range between ≈ 1 and ≈ 1.6 Å.

In effect, in bcc Mo the $4d$ bonding states which dominate photoemission spectra[1] have mainly $d_{xy+yz+zx}$ nature, and the orbitals pointing in the bcc directions are considerably compressed with respect to the free atom, taking energetically advantage of the accumulation of bonding charge midway between the Mo atoms.[15] The half-distance between nearest neighbors (1.36 Å) corresponds in the free atom to a point in which ψ_{4d} is still very large ($\cong 0.5$ of its maximum), so that the long-range behavior of the atomic ψ is completely washed out in bcc Mo, in contrast to the behavior of the $4d_{z^2}$ orbitals in MoS_2. As a consequence, the entire behavior of the σ is dramatically distorted with respect to the free atom. The compression of the $4d$ states in the solid can be estimated by comparing the bcc charge densities by Zunger, Kerker, and Cohen[15] with the atomic HFS wave functions by Hermann and Skillman.[14] The peak of $|\psi|^2$ is shifted 40% towards smaller distances, and this suggests a shift in the solid of the Cooper minimum of about a factor of 2 to higher $h\nu$ in free-electron final-state approximation. This is qualitatively in agreement with the experimental results which show a shoulder reminiscent of the Cooper minimum around 180 eV.

Before concluding, we want to emphasize that the above arguments are only qualitative. At present the interesting point is that this approach gives a consistent connection between the measured cross sections and what is known about the d states in Mo and in MoS_2. Nevertheless, the validity limits of this approach are yet to be investigated; this will require a considerable theoretical effort which could be stimulated by the present work.

In conclusion, we have shown that the same atomic orbitals in different solids can have very different energy dependence in their photoionization cross sections, and we have suggested a connection between the $h\nu$ dependence of the cross sections and the nature of the bonds in the solid state.

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