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3p resonance photoionization of the valence band in metallic Ca: Atomic and solid-state many-body effects

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The valence-band photoemission of metallic Ca is shown to be resonantly enhanced in the region of 3p excitation. The general shape of the resonance profile can be explained as an atomic phenomenon, namely, a 3p-3d giant dipole resonance driving the valence-electron photoionization process. The metal aspects are revealed by the shape of the resonance, the asymmetry of which reflects the 3d character of the valence band, and by additional structure, which probably represents a coupling to shake-up processes.

The excitation of p-like core electrons into empty valence orbitals in transition metals gives rise to resonances in optical absorption and ionization spectra which exhibit various kinds of many-body effects.[1,2] In this Rapid Communication we report a study of the 3p resonance in calcium metal comprising the measurement of the valence-band (VB) photoemission intensity in the vicinity of the 3p threshold, and a calculation of the 4s-, 3d-, and 3p-photoionization cross sections in a local-density-based random-phase approximation (RPA). Achievements and shortcomings of the theory become apparent.

Calcium immediately precedes the 3d transition metals, and free calcium atoms do not have any 3d electrons in the ground state ($4s^2 3d^0$). Metallic calcium, on the other hand, does have some 3d character in the ground state owing to hybridization with d bands above the Fermi level, approximately 0.5 3d electrons according to band-structure calculations.[3] Our RPA calculation using a configuration appropriate for the metal, $4s^{1.5}3d^{0.5}$, strongly suggests that the photon energy dependence of the experimental VB intensity indeed shows the signature of 3d emission, namely, a low-energy interference minimum followed by a maximum. The experimental data show an additional maximum at higher energies the explanation of which requires a refinement of the theory.

Experiments were carried out at the Hamburger Synchrotronstrahlungslabor HASYLAB using the grazing incidence monochromator FLIPPER.[4] Ca films were prepared by evaporation from tungsten baskets in the spectrometer chamber at a base pressure of 1×10^{-10} Torr. Figure 1 shows a typical energy distribution curve (EDC) of the valence band at 62 eV photon energy. The valence-band photoemission intensity as a function of photon energy was obtained by "constant initial state" (CIS) spectroscopy, the initial energy being set to the valence band (0.5-eV window centered 0.3 eV below the Fermi level). The measured spectra were normalized to the photon flux and to the variation of the analyzer transmission.[5] It should be mentioned that all features to be discussed below are clearly discernible in the raw spectra so that they are not artificially introduced by the normalization procedure.

Figure 2 shows the result for the VB photoemission intensity. Because of the difficulties associated with the treatment of photoemission in a solid as a one-step process, we discuss this spectrum in terms of photoionizaton cross sections. In the limit of separate probabilities for an electron to be ionized and to leave the solid without being scattered inelastically, it has been shown that the escape probability is essentially structureless for energies exceeding the threshold energy by more than 20–30 eV.[5,6] The minimum in the valence-band intensity profile at 25 eV and the maximum at 33 eV can be described in terms of an atomic $3p \rightarrow$ "$3d$" resonance excitation, a $^1S_0 \rightarrow {}^1P_1$ giant dipole resonance,[1,2,7] ionizing the 3d-like valence electrons. This indicates that the observed structures can safely be attributed to the photoexcitation probability.

The resonance profile of the VB photoionization cross section in Fig. 2 can be understood within an atomic framework, using a mean-field approach like the random-phase approximation (RPA) for describing the dynamic response

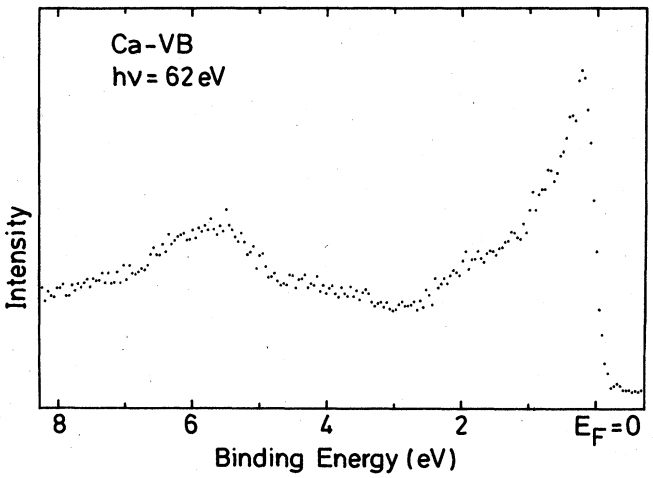

FIG. 1. EDC of the valence band of metallic Ca at 62 eV photon energy.

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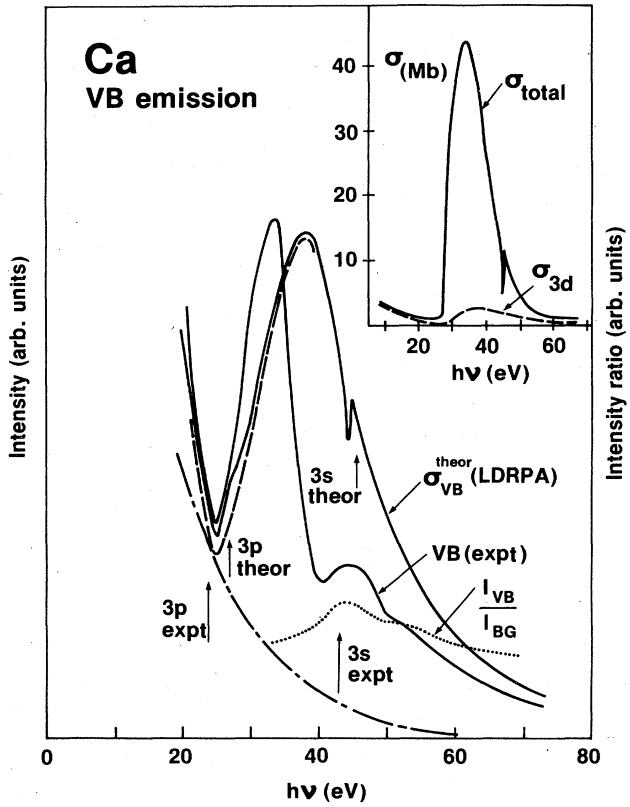

FIG. 2. Experimental valence-band (VB) photoemission intensity for Ca metal, compared with a local-density based RPA calculation (LDRPA). The orbital occupation is $4s^{1.5}3d^{0.5}$ (however, atomic potential based on $4s^23d^0$) and the VB cross section is constructed as $\sigma_{VB}^{theor}=0.15\sigma_{3d}+0.06\sigma_{4s}$ (dashed curve: σ_{3d} alone) where σ_{3d} and σ_{4s} refer to cross sections per electron. σ_{VB}^{theor} is superposed on a background (dashed-dotted curve) which may give a rough idea about the magnitude of solid-state effects. The maximum value of the atomic-like cross section is ~ 2.5 Mb at ~ 38 eV photon energy. The inset shows the total LDRPA cross section in the 10–70 eV range (the $3d$ cross section shown for comparison). The dotted curve represents the intensity ratio between a CIS spectrum of the VB and a CIS spectrum of the background (BG) at 5.5-eV binding energy.

of the coupled atomic shells. The present calculation is based on a diagrammatic expansion of the photoionization amplitude (polarizability, bubble diagrams) evaluated using a local-density approximation (LDA) for the atomic potential and wave functions. This approach (LDRPA)[1,8] is similar, but not identical, to the time-dependent local-density approximation (TDLDA).[9,10] We actually use a potential corresponding to the atomic ground-state configuration $3s^23p^64s^23d^0$. However, when calculating induced potentials and photoionization amplitudes and cross sections, the configuration was chosen as $4s^{1.5}3d^{0.5}$ to simulate $3d$ occupation in the ground state of Ca metal. The LDA potential used here[11] does not have any long-range Coulomb tail and might be said to simulate some properties of the screened core hole potential in a metal. The effective potential has an inner-well region supporting $3d$ orbital,[12] followed by an angular momentum barrier. At larger distances the potential remains positive and slowly tends to zero. There is consequently no outer-well region supporting Rydberg levels. In the one-electron approximation the excitation spectrum is, therefore, characterized by a discrete $3p \rightarrow 3d$ resonance below the $3p$ threshold and a weak continuum above. However, taking into account the very large dynamic polarizability of the $3p$ shell, giving rise to a large induced field, the $3p \rightarrow d$ oscillator strength appears as a continuum resonance (giant dipole resonance, "collective resonance"[2]). This may also be thought of as a $3p^53d$ resonance shifted to above the $3p$ threshold and escaping into the continuum.[1,2,13,14]

The resulting total photoionization (photoabsorption) cross section is shown in the inset in Fig. 2 and is clearly dominated by the $3p \rightarrow$ "$3d$" giant dipole resonance in the $3p \rightarrow d$ continuum cross section. Although broad, this resonance gives rise to Fano-type asymmetric resonance profiles in the $3d$ and $4s$ emission channels: The $3d$ emission has an interference minimum in the region of onset of $3p$ absorption and a maximum around 38 eV, while the $4s$ emission has a maximum around the $3p$ threshold and a minimum around 50 eV. This is analogous to the result found by Zangwill and Soven[9] in the case of $4f$ and VB emission in the $4d$ region in cerium. We have also calculated the $4p$ cross section which is similar in shape to, but considerably smaller than, the $4s$ cross section in the region of the $3p \rightarrow$ "$3d$" giant dipole resonance.

To compare the experimental VB emission with theory we infer from calculated partial densities of states[15] that 0.15 $3d$ electrons, 0.18 $4p$ electrons, and 0.06 $4s$ electrons are contained in a 0.5-eV-wide interval below the Fermi level. Neglecting the $4p$ contribution due to the low cross section in the region of the $3p$ resonance we construct a theoretical valence-band cross section $\sigma_{VB}^{theor}=0.15\sigma_{3d}+0.06\sigma_{4s}$, where σ_{3d} and σ_{4s} are cross sections per electron. σ_{VB}^{theor} has finally been properly scaled and superimposed on a smooth but rapidly varying background, and the result for σ_{VB}^{theor} and also σ_{3d} alone (dashed curve) are shown in Fig. 2. From the quite reasonable agreement between theory and experiment we conclude that the photon-energy variation of the experimental VB intensity in the $3p$ resonance region shows the signature of $3d$ emission.

On the low-energy side of the $3p \rightarrow$ "$3d$" resonance maximum (Fig. 2), there is a particularly large discrepancy between the measured VB intensity in the metal and the calculated intensity from the LDA atom, revealed by the steep rise in the assumed background. However, this is hardly surprising. In a realistic calculation, one might take the effective driving field from an atomic LDA-based mean-field calculation but one would have to use initial and final one-electron states from a band calculation. The atomic calculation should then be done with a valence configuration similar to that of the metal, e.g., $4s^{1.5}3d^{0.5}$. In addition, collectivelike modes of the valence electrons would have to be taken into account.

On the high-energy side of the $3p \rightarrow$ "$3d$" resonance the measured cross section of the metal exhibits an additional minimum and maximum, and it is difficult to relate these structures to excitations of atomic origin. Structure in this region has indeed been observed in photoemission of atomic Ca: The prominent satellite structure in the $3p$ core-level spectrum is connected with important double, and even triple, excitations in absorption,[7] leading to sometimes dramatic variations of the intensities of the $4s$ and $3p$ lines and their satellites in the 35–80 eV range of photon energies.[16,17] There is a correlation between the $3s$ threshold in

the metal and the additional oscillation. In the calculation, however, the 3s channel, including a $3s \rightarrow 4p$ window resonance, does not seem to give rise to sufficiently intense structure to be important in the metal. We conclude that the high-energy structure accompanying the valence-band resonance most likely is characteristic for Ca metal.

We have also monitored EDC's of the valence-band photoemission in the photon-energy range of 3p-resonance. For photon energies near the second resonance maximum at 45 eV we observe a significant change in the relative intensity of the valence band compared with the emission intensity at higher binding energy. Here, most of the intensity originates from inelastically scattered secondary electrons; however, some weak satellite structures may also be present. Unfortunately, the photoemission in the binding-energy region between 5 and 10 eV was found to depend on the sample preparation so that we are unable to extract the intrinsic valence-band loss structure from our measured spectra. Instead, we have measured CIS spectra of the emission behind the valence band to which the CIS spectrum of the valence band can be normalized. The result for a CIS spectrum taken at 5.5 eV below E_F is represented by the dotted curve in Fig. 2, a similar result was obtained at an initial energy of 3.9 eV below E_F.

We find that the intensity ratio between the valence-band photoemission and the "background" shows a maximum at 45 eV and an indication of a shoulder at higher energy in close correspondence with the features of the valence-band cross section above 40 eV. Below and above these features the intensity ratio shows the same value. Very similar results have been obtained for the following 3d transition metals Sc through Cr for which an even more dramatic additional maximum in the valence-band cross section accompanies the 3p resonances on the high-energy side.[18] This lends support to the interpretation of the described effect as intrinsic also for Ca in spite of the fact that the shape of the valence-band loss structure showed some variations from sample to sample in EDC's. Note that these variations occurred even below the detection limit of specific impurities by Auger or photoemission techniques.

The observed change in the relative intensity of valence-band and "background" emission suggests that 3p core states which are resonantly excited around 45-eV photon energy do not only decay into single-hole valence-band final states, but also into more complicated valence-band satellite excitations. It is tempting to associate also the resonantly excited 3p core states with satellite excitations, especially since very intense satellite structures have been reported for x-ray excited 3p photoemission spectra of Ca metal.[19] These satellites have been attributed to intrinsic excitations of plasmons although the unusually strong intensity relative to the main 3p line could not be explained.[9] The investigation of plasmon coupling to core excitations is indeed very difficult in Ca, since the free-electron-like behavior is distorted by the presence of the d bands at the Fermi level.[6] On the other hand, the satellites must not be entirely attributed to plasmons and, moreover, the entire 3p core-hole spectrum may have to be discussed in terms of differently screened holes, or even in terms of a term-level type of structure of the 3p hole interacting with a 3d-like screening charge. A calculation taking proper account of the Ca band structure and core-hole screening is probably necessary for a satisfactory description of the 3p XPS spectrum of Ca metal and may be essential also to describe the dynamics of the 3p giant dipole resonance region.

It is of particular importance to analyze the resonance photoemission problem in the 3p and 2p regions simultaneously.[1] Barth, Gerken, and Kunz[20] have recently obtained the total absorption spectrum and the valence-band resonance photoemission of Ca metal,[20] to which we refer for comparison. In contrast to the 3p-"3d" giant dipole resonance, which carries a large part of the total oscillator strength of the 3p shell, the $2p \rightarrow 3d$ white lines only carry a small fraction of the 2p oscillator strength. Moreover, the 3d wave function is more localized in the 2p-3d excitations than in the $3p \rightarrow$ "3d" excitation, where it really corresponds to a continuum resonance, and the decay channels and interaction strengths are different for the two cases. The atomic LDRPA seems to work quite well also in the case of the 2p resonance, provided that the 2p Auger width is taken into account. Preliminary results[21] give a $\sim 1{:}1$ intensity ratio of the white-line spin-orbit partners, the $J = \frac{1}{2}$ line being slightly broader and more asymmetric than the $J = \frac{3}{2}$ line. Asymmetric resonances are found in all partial cross sections, the 4s and 3s cross sections having interference minima on the high-energy side of the resonance and the 3d and 3p cross sections on the low-energy side. The preliminary results suggest that the experimental VB intensity variation with photon energy does not show any clear 3d or 4s, 4p signature. However, a strong 4s, 4p emission seems to be evident, possibly consistent with the large width of the electron spectrometer window (~ 2.5 eV, Ref. 20).

In conclusion, we have investigated the 3p-3d resonance of calcium metal by means of resonant photoemission technique and local-density based RPA calculation. The major resonance of the valence-band emission in the region of the 3p threshold is found in good agreement with the calculation for the 3d emission intensity. On the high-energy side of this resonance, additional structure is observed which cannot be described by the present mean-field single-excitation calculation. The analogy of this structure with features observed in the 3d transition metals Sc through Cr are planned to be the subject of a forthcoming publication.[18]

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