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Collapse of the 4*f* wave function in cesium

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The collapse of the 4*f* wave function in various Cs systems was studied by means of inverse photoemission (IPE). At about 10 eV above the Fermi level, the ionic compounds CsI and CsO_x display sharp IPE spectral structures that are attributed to Cs $4f^1$ electron-addition states, but no 4*f* signal is found in the case of Cs metal. These observations provide strong evidence for a collapse of the 4*f* wave function in ionic compounds; this collapse is caused by charge transfer from Cs to the anions.

The collapse of the 4*f* wave function is a topic that has been discussed controversially for many years among atomic and solid-state physicists.[1–5] For the lanthanides and a few elements preceding them in the Periodic Table, the radial many-body potential for 4*f* electrons in a free atom can be described by a double-well structure.[1] The wells are separated by a potential barrier originating from competition between nuclear attraction, electron correlation, and centrifugal repulsion. As pointed out in pioneering work,[2,6] solutions of the radial Schrödinger equation in a double-well potential tend to transfer suddenly between the outer and the inner well for relatively small changes in the height of the barrier separating the two wells (wave-function collapse).

For the ground state of neutral atoms with atomic numbers $Z \leq 56$, the 4*f* wave function resides mainly in the outer well, penetrating the barrier only slightly, while for $Z \geq 58$, the 4*f* states become localized in the inner well. The sudden contraction of the 4*f* wave function occurs at about $Z = 57$ (La).[7] The picture is more complicated in solids, where an overlap of the potentials of neighboring atoms can strongly affect the interwell barrier as well as the shape of the outer well resulting in a bandlike character of the noncollapsed electronic states. Even in the case of metallic Ce ($Z = 58$), there is a set of experimental[8,9] and theoretical[10] evidences for localized or more bandlike 4*f* orbitals in γ-Ce and α-Ce phases, respectively, although this point is still discussed in a controversial way.[11,12]

A collapse of the 4*f* wave function can also be induced by ionization or by electron excitation. For the ground state of Ba^+, for example, a hybrid function composed of collapsed and noncollapsed states has been predicted.[3] In the case of Cs^+, experimental evidence has been given by Auger spectroscopy for a transition from uncollapsed 4*f* orbitals in I^- (as in KI) to collapsed 4*f* states in Cs^+ (as in CsCl).[4] Evidence for a wave-function collapse when going from Cs metal to Cs halides has also been provided on the basis of x-ray absorption spectra.[5,13,14] These latter results are in good agreement with theoretical considerations,[15] illustrating the sensitivity of the radial potential on the removal of an outermost *s* electron. However, since both the Auger and the x-ray absorption experiments include the creation of deep core holes, which strongly affect the many-body potential involved, no direct conclusions on ground-state properties can be drawn from these experiments. A better probe for the ground state is the direct transfer of a free electron into the 4*f* orbital as occurring in inverse photoemission (IPE). As shown recently for La metal, such a direct observation of unoccupied 4*f* states is even possible for rather low electron energies.[16]

In the present work we report on an IPE study of Cs metal and of the ionic compounds CsI, CsO_x, and RbI. For CsI, the IPE data show a sharp structure at an energy of about 10 eV above the Fermi level E_F which is not observed in the corresponding spectrum of RbI; this feature is assigned to a $4f^1$ electron-addition state. The same structure is observed in the IPE spectrum of CsO_x, while no 4*f* signal could be detected in the case of Cs metal. This suppression of a 4*f* IPE signal is explained by a transition of the 4*f* wave function from the inner to the outer well, caused by screening of the nuclear potential through conduction electrons.

The experiments were performed with a home-built IPE spectrometer[17] operating in the photon-energy range from ≅ 9 to ≅ 32 eV, with a total-system resolution of 0.4 eV (full width at half maximum) at $h\nu \cong 20$ eV. The vacuum in the experimental chamber was better than 2×10^{-10} mbar during the measurements. Thin films of CsI and RbI (≅ 60 Å thick) were prepared by *in situ* deposition of the materials from an indirectly heated quartz crucible onto a Ta foil at room temperature; during deposition, the pressure in the chamber was $\cong 8 \times 10^{-10}$

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mbar. Coverages were calibrated by a quartz microbalance with an estimated accuracy of ±20%. Cs films were deposited from commercial chromate dispensers onto a liquid-nitrogen-cooled Ta substrate. The formation of CsO_x layers was achieved by deposition of Cs metal ($\cong 5$ ML; deposition rate $\cong 1$ ML/min) in an oxygen atmosphere of 1×10^{-7} mbar.[18]

Inverse photoemission spectra were taken in the constant-initial-state mode for primary-electron energies E_p varying between 17 and 25 eV. In order to prevent charging of the insulators as well as electron-induced surface metallization of the alkali-halide compounds,[19] primary electron currents less than 5 μA were applied. Since such low electron currents result in long data acquisition times ($\cong$ 4–6 h per spectrum), the samples were freshly prepared after every 2 h of data taking. During these time spans, no changes in the spectral features for a given sample were observed.

An overview IPE spectrum of CsI, taken with a primary electron energy E_p=22 eV in the energy range up to $\cong$ 14 eV above the Fermi level, is shown in Fig. 1(a). As discussed in Ref. 20, the three low-energy features A, B, and C stem from unoccupied bands with d symmetry, while peak F can be assigned to radiative decay of plasmons. This assignment was based on the plasmon energy of CsI (Ref. 21) and the dependence of the energy of peak F on E_p. In the following we shall concentrate on the spectral region built up by the other two prominent features D and E displayed on an expanded scale in Fig. 1(b). Since the energies of these two features do not vary with E_p, they can be attributed to the unoccupied density of states of CsI. For comparison, we present in Fig. 1(c) the analogous IPE spectrum of the isostructural compound RbI, which is isoelectronic to CsI except for the 4f states. Both spectra contain the same broad emission feature E, but the sharp structure D is missing in the spectrum of RbI. We therefore assign it to a Cs $4f^1$ electron-addition state.

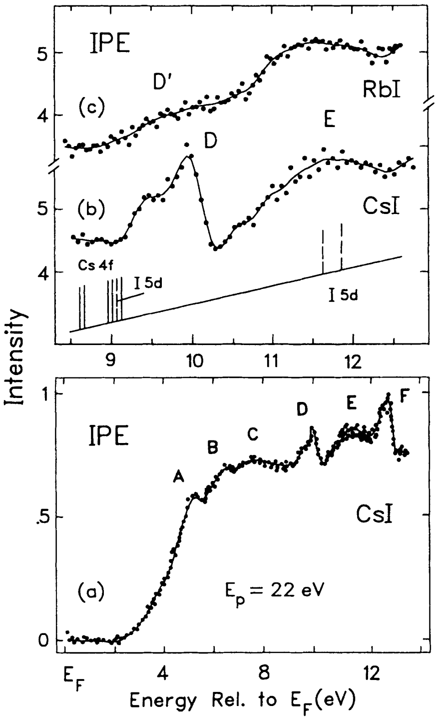

FIG. 1. (a) Overview IPE spectrum of CsI taken for a primary-electron energy of E_p = 22 eV. (b) and (c) show IPE spectra of CsI and RbI, respectively, on an expanded energy scale. Energies of "d-" and "f-symmetry" critical points in the band structure of CsI (Ref. 22) are marked by bars in the center of the figure. Cs-derived critical points represent pure f character.

The bar diagram underneath Fig. 1(b) marks the energies of the critical points in the electronic structure of CsI as obtained from a relativistic band-structure calculation.[22] To adjust the energy scales, the Fermi level of the calculated band structure was placed in the middle of the band gap. In this way the broad feature E in Fig. 1(b) can be assigned to electronic states with d symmetry located predominantly at iodine sites. In the region of structure D, mostly Cs 4f states are expected. A dispersing d-like iodine-derived band (dashed bar at $\cong$ 9 eV) does not significantly contribute to the IPE spectrum of CsI, and appears only as a broad structure D' in the spectrum of RbI [Fig 1(c)]. The observed 1-eV shift of feature D towards higher energies as compared to the calculated energies of the 4f band can be explained by the strongly correlated nature of the 4f states, causing a breakdown of the single-particle picture and the formation of an atomiclike 4f multiplet in the final state. Note that peak D shows a clear splitting into two components separated from each other by about 0.4 eV. This is much larger than the expected spin-orbit splitting of an atomiclike Cs $4f^1$ configuration [for La the $4f^1$ spin-orbit splitting amounts to 186 meV (Ref. 23)], but is nearly equal to the calculated splitting of the 4f bands.[22] This leads one to the assumption that the $4f^1$ final state has bandlike character.

A completely different situation is observed for Cs metal. The corresponding IPE spectrum recorded in the wide energy range up to 12 eV above E_F is presented in the inset of Fig. 2. As shown previously in studies of thin Cs films in the energy range close to the Fermi level,[24,25] the photon intensity attributed to transitions

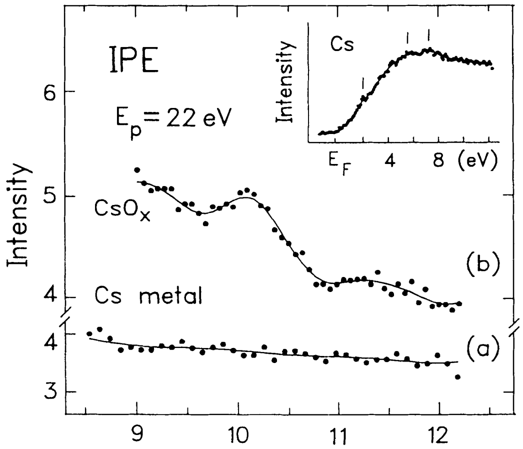

FIG. 2. IPE spectra of (a) Cs metal and (b) CsO_x taken for a primary-electron energy of E_p = 22 eV. The inset gives the overview spectrum of Cs metal.

into unoccupied states of 6*s* and 6*p* symmetry is very weak. The prominent increase in the IPE yield $\cong$ 2 eV above E_F has been assigned to the decay of a 2-eV plasmon in metallic Cs. While the heavy alkali metal cesium is in fact a *d*-band metal with a strongly structured unoccupied density of states,[26,27] the aim to observe *d* bands was almost totally missed by the dominance of inelastic effects. Only one weak feature at $\cong$ 1.5 eV binding energy was attributed to a transition into electronic states with *d* character.[24]

In addition to this low-energy structure, the overview IPE spectrum of Cs metal (inset in Fig. 2) contains two other broad features at energies of $\cong$ 5.5 and $\cong$ 7 eV above E_F (marked by vertical bars), which can be assigned to *d* bands as calculated in the work of Ref. 27. Except for these weak peaks no other structures can be identified. Particularly in the energy region, where states with 4*f* symmetry are expected, the spectrum is absolutely flat and structureless. Figure 2(a) shows the corresponding spectral region on an expanded scale. Oxidation of Cs metal leads again to the appearance of a peak at $\cong$ 10.2 eV shown in the spectrum of Fig. 2(b). As compared with the $4f^1$ emission in CsI, this structure is shifted by 0.5 eV to higher energies. Similar shifts have been observed for Cs core-level binding energies in the PE spectra of CsI and CsO_x.[18,28] These shifts are caused by the different chemical environment in these materials. Hence, we also atribute the 10.2-eV peak in the spectrum of CsO_x to a $4f^1$ electron-addition state.

The suppression of a 4*f*-related IPE signal in Cs metal can be explained by a transition of the 4*f* wave function from the inner to the outer well caused by a change in the screening of the effective nuclear potential by conduction electrons. As can be seen from the free-atom calculation of Ref. 15, the width of the radial wave function in the outer well ($\cong$ 15 Å) is large compared to both the de Broglie wavelength of the incident electrons ($E_p = 22$ eV) and the interatomic distances in Cs metal. The rapid oscillations of the primary-electron waves as compared to the weakly varying noncollapsed radial 4*f* function quenches the overlap integral between the initial- and final-state wave functions. This results in a low cross section for transitions into the extended 4*f* state. In addition, the large overlap between the neighboring noncollapsed 4*f* orbitals in Cs metal will lead to a strong broadening of the 4*f* bands. Both the low cross section and the large bandwidth of the noncollapsed 4*f* electronic states explain the quenching of a sharp 4*f*-derived feature in the IPE spectrum of Cs metal. On the basis of the above considerations, we speculate that the IPE signal from the anomalously dispersed 4*f* electronic states contributes to the wide background in the energy region from 2 to 8 eV, which was previously solely assigned to plasmon decay.[24]

Note that in contrast to the Cs 4*f* states, the potential for Cs 5*d* wave functions, calculated by taking valence-core-electron exchange interaction into account, does not possess a double-well character.[29] If the interwell barrier is low or absent, then even an inner well, which is not large enough to support an isolated bound state, can cause a significant contraction or partial collapse of the orbital. This situation explains the appearance of 5*d*-derived structures in the IPE spectrum of Cs metal, while 4*f* electronic states are not observed there.

Upon oxidation of Cs metal, valence electrons are transferred to anion sites and the resulting increase in the local core potential leads to a collapse of the 4*f* orbitals. In this case, the width of the collapsed 4*f* wave function is smaller than the interatomic distance and of the same order of magnitude as the wavelength of the incident electrons. Transitions into these more localized 4*f* states lead to the appearance of a $4f^1$ IPE signal as observed in the spectrum of CsO_x.

In summary, we have shown that the $4f^1$ wave functions are already collapsed in the ionic compounds CsI and CsO_x, while they are extended and delocalized in Cs metal. This phenomenon is explained by a screening of the nuclear potential through conduction electrons in the case of Cs metal.

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