Origin of the Two-Peak Photoemission and Inverse-Photoemission Spectra in Ce and Ce Compounds

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The origin of the two-peak photoemission and inverse-photoemission spectra in Ce and its pnictide compounds (CeP, CeSb, and CeN) is investigated with *ab initio* total-energy self-consistent supercell energy-band and molecular-cluster approaches to represent physically the competing mechanisms involved in d or f electron screening (antiscreening in the case of inverse photoemission) of the local $4f$ electron excitations. Good agreement with experiment is obtained in all cases including the "anomalous" case of CeN.

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The nature of the $4f$ electron and its role in the electronic structure of cerium and its compounds has generated substantial experimental and theoretical interest. Key questions include possible mixed-valent properties, Kondo-lattice behavior, and the role of f-d hybridization or correlation on the ground- and excited-state properties. A matter of considerable controversy has been the origin of the observed double peak in photoemission spectra arising from the $4f$ states. In Ce metal, the two peaks (at and below the Fermi energy, E_F) are separated by[1] 2 eV. Except for CeN, the cerium pnictides show very similar photoemission spectra which are characterized by a $4f$-related peak near E_F (~ 0.6 eV below) and one located at 3.0–3.1 eV below E_F. In CeP, the peak at E_F is dominant in intensity, but by the time one reaches CeSb the peak at -3.1 eV is dominant.[2,3] The spectrum of CeN is more complicated[4]: There is a strong f peak at about -0.35 eV and another f peak at -1.2 eV which is thought to be due to a surface state; there is also another feature at -5.5 eV that is probably f related. A two-peak structure is also seen in the inverse-photoemission (BIS) spectra of Ce[5] and several cerium compounds.[6]

The interpretation of the two-peak photoemission structure has generally focused on either many-body ground-state[7,8] or final-state[9–12] effects in the excitation process itself but to date no quantitative proof has been given of the validity of either approach. Here we present results of self-consistent local-density electronic structure calculations which focus on the different mechanisms for screening the local $4f$ hole in photoemission and antiscreening the additional $4f$ electron in BIS. In order to ascertain the validity of the results obtained, we minimize their dependence on the method used by employing three different theoretical approaches: (i) total-energy molecular-cluster studies of metallic Ce, (ii) total-energy supercell energy-band-structure studies of metallic Ce, and (iii) transition-state supercell studies of several cerium pnictide compounds, CeP, CeSb, and CeN. The agreement between the calculated energy separations of the resulting two-peak structure with both photoemission and BIS experiments lends strong support to their origin as being final-state effects.[9–12]

We assume that in the photoemission (inverse photoemission) process a local single-atom $4f$-orbital excitation is screened (antiscreened) differently by different channels: f electrons provide full screening whereas d-conduction electrons only partially screen (antiscreen) the f hole (electron).[10,11] This is in keeping with the observation that a well screened, poorly screened model has provided a very successful interpretation of the systematics of core-level spectroscopies in transition-metal compounds.[13] To a first approximation, the f-screened hole is described by the results of a ground-state calculation. In the poorly screened process, the $4f$ hole remains unoccupied and can be simulated by self-consistent local-density molecular-cluster or supercell approaches in which the resultant "impurity" site is screened by the conduction electrons. Similarly, in BIS the extra $4f$ electron is *antiscreened* by either a $4f$ electron or a d-conduction electron, i.e., the depletion of d or f charge on the site.

The molecular-cluster approach was applied to nineteen Ce atoms in an fcc structure with the γ-Ce lattice constant. The electronic structure was determined self-consistently by use of a total-energy, discrete, variational, linear combination of atomic orbitals approach.[14] In the ground state the $4f$, $5d$, and $6s$ valence orbitals were occupied with 4 electrons and the core electrons (up to $5p$) were kept frozen. To treat the localized f-hole state, we use an ionic Ce^+ basis set with the $4f$ orbital unoccupied for the central atom; for the outer eighteen atoms (nearest and next-nearest neighbors) a neutral Ce^0 basis with $4f$ occupied by one electron is employed. In the self-consistent procedure the cluster is electrically neutral but the $4f$ orbitals on the central site are kept unoccupied in order to maintain a localized $4f$-hole on the central site Ce atom. The screening charge surrounding the $4f$ hole is found to arise predominantly from the $5d$ electrons. The well-screened case is obtained by a separate self-consistent calculation in which the central $4f$ hole is allowed to be reoccupied by f electrons during the self-consistent iterations. The calculated total-energy difference between the two cases is 1.9 eV—in good agreement with the observed[1] photoemission peak located about 2 eV below E_F.

Total-energy, self-consistent, scalar, relativisitic, linearized muffin-tin-orbital (LMTO) supercell calculations in the atomic-sphere approximation (ASA) were employed as an alternate method to study the photoemission and BIS spectra in α-Ce and γ-Ce. In the photoemission case, the f state on the central site in supercells of up to eight atoms was forced to be unoccupied by omitting the $l=3$ radial function on this atom. We found that the ASA results in too strong a hybridization of the $4f$ electrons when they are treated as band states. To correct for this, the single $4f$ electron was treated as a core state, thereby effectively removing all this hybridization.

The calculated difference in total energy between the poorly and fully screened states is 1.9 eV for α-Ce and 2.4 eV for γ-Ce—again in qualitatively good agreement with the observed positions of the two peaks in the photoemission spectrum. The reversal of splittings in α and γ phases between theory and experiment[1] may be due to use of paramagnetic state results for γ-Ce and the fact that our various LMTO-ASA approximations are poorer for the contracted lattice constant in α-Ce. Surprisingly, the total-energy difference between this excited state and the ground state and details of the screening charge density (found again to be $5d$-like) are insensitive to the size of the supercell. Basically, all such properties are obtained even in a one atom per unit cell calculation which demonstrates the very local nature of the excitation.

The same approach can also be applied to the inverse-photoemission process since in BIS the extra electron forces charge away, resulting in an inverse-screening effect. The nature of the poorly antiscreened peak in the BIS spectrum was investigated by performing calculations which force the presence of two f electrons into the central cell. From the difference in total energy we predict poorly ($5d$) antiscreened peaks in the BIS spectrum at 3.6 eV for α-Ce and 3.1 eV for γ-Ce above the ground state (well-screened case). Comparison with BIS experiments[5] is difficult because the data show greatly broadened lines (by multiplet and crystal-field effects). These calculated values are subject to more uncertainty than are the photoemission results because the treatment of the two $4f$ electrons as core states is less exact. By combining the photoemission and BIS results, however, we find a value of 5.5 eV for the effective intra-atomic Coulomb interaction, which appears to be in good agreement with the experimental value[5,15] of ~ 6 eV obtained from photoemission and BIS data.

Self-consistent, warped-muffin-tin, scalar, relativistic, linearized augmented-plane-wave calculations (LAPW) were performed for the pnictides CeP, CeSb, and CeN. Spin-orbit coupling was included perturbatively at the end of the self-consistent iterations which employed 89 $\vec{k}$ points in the irreducible wedge of the (rock salt) Brillouin zone and an exchange-only potential (as this is thought to be most appropriate for f-electron systems). In all three compounds, we find E_F pinned near the bottom of the f bands, but no f electron structure at 3 eV (or at 5.5 eV) below E_F.

To study the case where a $4f$ hole is maintained on a central Ce atom, supercell calculations, with eight atoms per unit cell and (for equivalent convergence) an enlarged basis (515 LAPW's at Γ) compared with that for the ground-state studies (137 LAPW's at Γ), were employed. To simulate this hole, the $l=3$ energy parameter for the LAPW radial wave function of the central Ce muffin tin was set in the $5f$ energy region which effectively depopulated all of the f character out of this sphere. The system was then allowed to relax self-consistently, thereby incorporating screening of the f hole into the procedure.

The final iteration was run by putting the $l=3$ energy parameter back into the $4f$ energy region. This yields the eigenvalue dispersion of the f hole in the relaxed final state. The resulting excitation energy is obtained by use of a Slater transition-state analysis as an alternative to the calculation of total energies: With the assumption of a linear dependence of the eigenvalues on occupation number, the excitation energy is found as the average of the f-state eigenvalue in the ground state (at E_F) and its eigenvalue in the final poorly screened state. For CeP and CeSb, the f-hole states show up as an extremely localized feature below the bottom of the valence band. The transition-state analysis then yields energy shifts of 2.47 and 2.71 eV compared with the somewhat smaller experimental values of 2.4 and 2.5 eV, respectively. (This result is actually quite reasonable since too much f charge was removed in CeSb; the supercell procedure reduced the 1.2 electrons of f character down to 0.03 electron rather than the 0.1 electron as found in LaSb.) For the "anomalous" case of CeN (in which the poorly screened peak is apparently not observed) the f-hole states are delocalized over the entire valence band as a result of strong f-p hybridization (cf. Fig. 1). We thus conclude that a screened f hole does not exist in CeN and hence should not be (and is not) observed.

The same techniques were also used to derive the two-peak structure also seen in the BIS spectra of several cerium compounds[6]—a peak at about 0.5 eV above E_F and another peak at about 4–5 eV above E_F. The ground-state band calculations show a large peak in the density of states just above E_F as a result of unoccupied f states. We identify this peak with the first peak in the BIS spectra and interpret it as the fully relaxed peak formed by the hopping away of the extra f electron introduced on the site. The second peak can be thought of as a localized $f^1 \rightarrow f^2$ transition, i.e., the final state is a two-f-electron bound state. To simulate this with supercell calculations, we move the $l = 3$ LAPW energy parameters for the central Ce site up into the $5f$ energy region but now place two f electrons in the core of the central site. (Thus, while these electrons are not allowed to hybridize they are otherwise treated exactly.) This system is then allowed to relax which results in depletion of d charge inside the central muffin tin via antiscreening. The unoccupied states are now reanalyzed with use of this new potential by replacing the $l = 3$ energy parameter back into the $4f$ energy region as described above. For CeP, this yields a transition-state derived peak at 4.4 eV which is analogous to the d-screened f hole in the photoemission calculation, but is now a d-antiscreened two-f-electron bound state. Combining the band and supercell results as before yields a spectra with a peak at 0.4 eV (band) and 4.4 eV (supercell)—very similar to the experimental spectra of various cerium compounds. (The BIS spectrum for CeP has not been done, but that experiment is now being planned.[16]) Our BIS results are thus a mirror image of our photoemission ones.

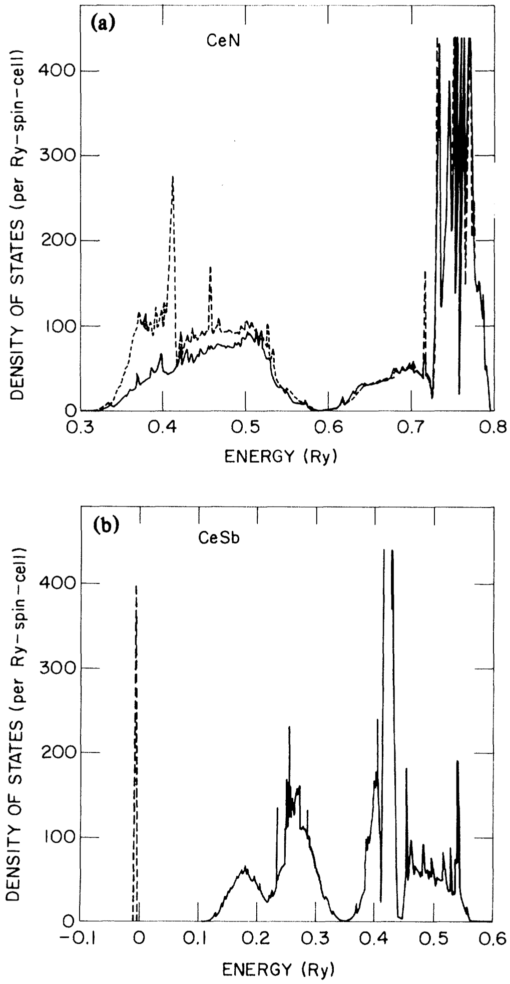

FIG. 1. Supercell density of states for (a) CeN and (b) CeSb (states per Ry per spin). The solid line is for the f-hole calculation. The dashed line is the result when the central-site f states are put back in (calculated with the f-hole potential). The supercell Fermi energy is at 0.6821 Ry for CeN and 0.2989 Ry for CeSb. The diagram for CeP looks similar to that for CeSb.

In conclusion, we have presented results of three different first-principles theoretical approaches to study final-state effects as the origion of the two-peak structure observed in both photoemission and BIS. The agreement of the results from the three approaches emphasizes their general nature and shows an insensitivity to the technique employed. The agreement with experiment lends credence to the validity of the fully screened, poorly screened model for describing the excitation spectra of Ce systems which has previously been invoked by several experimental groups.[10,11] Our interpretation of the the poorly screened peak agrees with that of Liu and Ho[12] but we differ with them on the origin of the fully screened peak which they attribute to screening by a collapsed *d* state. If one interprets the Gunnarsson-Schönhammer model a certain way,[17] then one can also find an equivalence between our approach and theirs. Finally, the results provide evidence for the general validity of the supercell approach for describing various excitation spectra.[18] To verify this, work on other systems besides cerium has been initiated.

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