PHYSICAL REVIEW B VOLUME 26, NUMBER 12 15 DECEMBER 1982

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Theory of photoemission from metallic Ce

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(Received 3 May 1982; revised manuscript received 21 July 1982)

It is shown that the two-peak structure of the $4f$ electron photoemission spectrum of Ce metal and its compounds may arise from two kinds of final states, those with and those without screening by a Ce $5d$ electron in an impurity state. A comparison between theory and experiment reveals that the γ-α phase transition is accompanied by a very slight increase in conduction-electron population.

The origin of the γ-α phase transition of Ce has been a controversial subject for many years. Both phases have the fcc crystal structure, but on going from γ to α the lattice parameter reduces by 6%.[1] Zachariasen and Pauling suggested that the volume collapse of the α phase is caused by the promotion of $4f$ electrons into the conduction band.[2] Based on this "promotion model," Ramirez and Falicov[3] showed that the explanation of the phase transition requires a narrow $4f$ level within 0.1 eV of the Fermi level. Early x-ray photoemission spectroscopy (XPS) experiments detected a $4f$ feature around 2 eV below the Fermi level.[4] In spite of this apparent conflict, all phenomenological models of valence instability assume a $4f$ level close to the Fermi level.

Johansson proposed a radically different model that in the α phase the f electrons somehow form a band and contribute directly to crystal bonding.[5] This "Mott transition" model is successful in estimating the cohesive energy of α-Ce. In addition, it predicts no significant change in the f population at the transition, in agreement with positron annihilation,[6] Compton scattering,[7] and neutron scattering[8] experiments. The success of the f band model has stimulated *ab initio* band calculations of both phases of Ce. Glötzel[9] obtained a broad f band for α-Ce, but a ground state with local moments of one f electron per atom for γ-Ce. On the other hand, the band theory cannot be reconciled with the XPS data because the theory put the f band very close to the Fermi level.[10] Any attempt to put it much below the Fermi level would result in unrealistic values of f occupation.

Hirst put the criterion for valence instability in a very succinct form, namely, that the total energy of the f^n configuration should be nearly equal to that of $f^{n-1}d$.[11] There have been two independent estimates of the difference in energy of the two configurations. Herbst *et al.*[12] calculated it by the renormalized atom method for the entire rare-earth series. Johansson[13] accomplished the same goal by using thermodynamic arguments and experimental binding energies of free atoms and metallic solids. The two estimates are in close agreement, and they both agree with the $4f$ binding energy measured by photoemission. For Ce the theoretical value for the binding energy is 2 eV, which is much too large for interconfiguration fluctuation to occur. In a later paper, Johansson[14] pointed out that both theoretical estimates neglected an "impurity" contribution E^{imp}, which is the further energy adjustment when a tetravalent cell fully relaxes in a trivalent environment. He estimates E^{imp} to be about -0.2 eV for all rare earths, not enough to make Ce satisfy the Hirst criterion for mixed valence. Therefore, the fact that Ce is mixed valent argues strongly that E^{imp} was underestimated for Ce.

Recently, new experiments on Ce systems have been performed using synchrotron radiation and improved materials preparation techniques. In addition to the 2-eV feature, a new peak is seen very close to the Fermi level.[15,16] Furthermore, there is little difference in the spectra of the two phases of Ce.

It is well known that the photoemission spectra of inner-shell electrons may have more than one peak.[17,18] The satellites are associated with shake-up and shake-down processes involving a change of population of an outer shell in the final state. In the shake-down process an electron is added to an outer shell to screen the core charge and, consequently, the emitted electron appears to have a lower binding energy. We will show that a similar process gives rise to the two-peak structure of Ce, and we identify the screening electron as Ce 5d in an impurity state. The theory of impurity state screening has been worked out by Davis and Feldkamp,[19] and we will adopt their analysis to the present situation. To a good approximation we treat the f electrons on different sites as independent and study the photoemission of one f electron at a time. The model consists of a bound f electron and a partially filled conduction band, which is of d character. The local f electron interacts with itinerant d electrons through the Coulomb repulsion. The Hamiltonian of the system is[19]

$$H = \sum_k \epsilon_k d_k^\dagger d_k + \epsilon_f f^\dagger f - \frac{U}{N} \sum_{kk'} d_k^\dagger d_{k'} f f^\dagger \ , \tag{1}$$

where d and f are the annihilation operators for the band and f electrons, respectively, N is the number of sites, U is the strength of the d-f Coulomb interaction, and ϵ_f is the energy of the f level. The d-f Coulomb interaction is expressed as an attraction between d electrons and the f hole so that the model energy band can be identified with the calculated bands for γ-Ce. We have suppressed the spin index for simplicity. The effects of d-band degeneracy will be discussed later. The f level is effectively nondegenerate because the strong intra-atomic Coulomb repulsion prohibits multiple occupancy.

The f^1 configuration problem is trivially solved. The ground-state energy of the system is

$$E_1 = \sum_{k,\mathrm{occ}} \epsilon_k + \epsilon_f \ , \tag{2}$$

where the sum on k is over the lowest N_d levels, N_d being the number of band electrons. The ground-state wave function is $f^\dagger \psi_1$, where

$$\psi_1 = \prod_{k,\mathrm{occ}} d_k^\dagger |0\rangle \ , \tag{3}$$

and $|0\rangle$ is the vacuum state. The solution of the f^0 configuration problem is also well known.[19] Consider the band states as a set of N closely spaced discrete levels, then the energies of the single-particle states are the N solutions of the equation

$$1 = (U/N) \sum_k (\epsilon_k - \omega)^{-1} \ . \tag{4}$$

The operator c_n for the new one-particle state with energy ω_n is given by a canonical transformation

$$c_n = \sum_k a_{nk} d_k \ . \tag{5}$$

There is a one-to-one correspondence between the new levels and the old ones such that each new level is shifted down slightly from an old level except the lowest one, which may shift down from the bottom of the band by an appreciable amount determined by the interaction strength, the band shape, and the bandwidth. In a simple model which has constant density of states extending from $-W$ to 0, the lowest state, which is pulled below the band, has the energy

$$\omega_1 = -W/(1-e^{-W/U}) \ . \tag{6}$$

This state has a wave function localized around the atom, and its occupation by a band electron screens the core charge due to the f hole. For N_d electrons in the band we obtain a complete set of many-body states

$$\phi_n = \prod_n c_n^\dagger |0\rangle \ , \tag{7}$$

with energies

$$E_n' = \sum_n \omega_n \ . \tag{8}$$

The sum or product on n is over the occupied levels. There are $N!/N_d!(N-N_d)!$ many-body states in this set.

In the photoemission process the intial state ψ_1 relaxes into the complete set of final states ϕ_n. The spectrum of the f electron is given by[17]

$$\rho_f(\epsilon) = \sum_n |\langle \phi_n | \psi_1 \rangle|^2 \delta(\epsilon - E_n' + E_1) \ , \tag{9}$$

where ϵ is the binding energy of the emitted electron. The matrix element is a determinant involving the coefficients a_{nk} in Eq. (5). The nature of the spectrum in Eq. (9), plotted in Fig. 1, has been extensively analyzed by Davis and Feldkamp.[19] The two peaks come from two classes of final states, i.e., those with the screening level ω_1 filled (low binding energy ϵ_1) and those with that level empty (high binding energy ϵ_2). The binding energies as measured from the peak positions are

$$\epsilon_1 = -\epsilon_f + \sum_{n=1}^{N_d} (\omega_n - \epsilon_n) \ , \tag{10}$$

and

$$\epsilon_2 = -\epsilon_f + \sum_{n=1}^{N_d} (\omega_{n+1} - \epsilon_n) \ . \tag{11}$$

The latter is the energy of the f state plus the sum of Hartree-Fock shifts of the occupied states due to the creation of an f hole. The separation between the

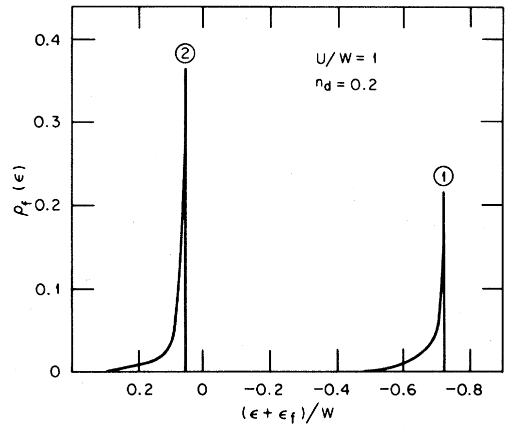

FIG. 1. The calculated photoemission spectrum of Ce, showing the two-peak structure.

two peaks is

$$\epsilon_2-\epsilon_1=\omega_{N_d+1}-\omega_1=\mu-\omega_1\ , \tag{12}$$

where μ is the Fermi energy.

The integrated intensity under $\rho_f(\epsilon)$ is unity, while that under the peak 1 is found to be

$$I_1=\langle\psi_1|c_1^\dagger c_1|\psi_1\rangle=\omega_1(W+\mu)/W(\omega_1-\mu)\ . \tag{13}$$

We find that the intensity I_1 increases rapidly as the band is more occupied or the Coulomb interaction is weakened. At the same time, Eq. (12) shows that the separation between the peaks increases with increasing band occupation through μ, and increases with increasing U through ω_1.

We now turn to the data in Ref. 16. The peak 1 is stronger in α-Ce than in γ-Ce. The separation between the two peaks remains unchanged through the phase transition. We conclude that α-Ce must have a slightly higher band occupation and a weaker d-f interaction. Taking $W=4$ eV[10] we find that the spectra can be simulated by $U=3.0$ eV, $n_d=N_d/N=0.15$ for γ-Ce and $U=2.8$ eV, $n_d=0.2$ for α-Ce. These values of U are reasonable for Ce.[20] The values of n_d are unreliable because of the multitude of simplifying assumptions in the model, but it is significant that n_d changes very little across the phase boundary. Any gain in band population must be compensated by a loss of f population. The intensities of the spectra at 120-eV photon energy,[16] at which the spectra are almost exclusively due to f electrons, indicate very little difference in f occupation between the two phases of Ce.

To relate our work to those of Herbst *et al.* and Johansson, we propose to identify ϵ_2 in Eq. (11) with the energy $E_{\mathrm{III,IV}}$ in Ref. 14, and $\epsilon_1-\epsilon_2$ with E^{imp}. The last step of the relaxation process is to fill the impurity level. Unfortunately, according to our picture, $E^{\mathrm{imp}}=-2$ eV, which is in strong disagreement with Johansson. When U is reduced so that $E^{\mathrm{imp}}=-0.2$ eV, the calculated spectrum exhibits only one peak as seen in other rare earths. On the other hand, it requires a large value for E^{imp}, approximately -2 eV, to make f^n and $f^{n-1}d$ configurations nearly degenerate in energy so that mixed valence can take place in Ce. Therefore the experimental facts are consistent with a strong local relaxation process which exists only in Ce. This mechanism, represented by the U term in Eq. (1), may be more complex than intra-atomic Coulomb interaction. Further studies are needed to unveil the nature of this interaction and to elucidate its effects on the mixed-valent properties of Ce systems.

ACKNOWLEDGMENTS

We wish to thank Dr. J. Weaver for suggesting this problem and Dr. L. C. Davis for many helpful discussions and criticisms during the course of the investigation. Oak Ridge National Laboratory is operated by Union Carbide Corporation under Contract No. W-7405-ENG-26 with the U. S. Department of Energy. Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This research was supported by the Director for Energy Research, Office of Basic Energy Sciences, WPAS-KC-02-02-02.

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