Effects of d-f correlation on the mixed-valence properties of cerium systems: The f-band problem

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The d-f correlation model, proposed by Liu and Ho to explain the double-peak photoemission spectrum of Ce, has been used to examine the f-band problem in Ce-based mixed-valence materials. The problem is solved in the spinless approximation and under the assumption that the f-level occupancy is nearly 1 on every Ce site. Two sets of d-f hybridized bands, corresponding to the two screening states of f^0 sites, have been found, and each set has two branches. At zero temperature, the upper branch of the upper set of bands has real energies, while all three other branches have complex energies. At finite temperatures, the quasiparticles in the upper branch also acquire a finite level width. This effect gives rise to a d-f interaction contribution to the electrical resistivity whose temperature dependence satisfies a simple scaling relation.

Liu and Ho proposed that the double-peak photoemission spectrum of Ce metal and some of its intermetallic compounds is a manifestation of a strong d-f interaction such that the emission of a $4f$ electron from a Ce site profoundly alters the local electronic structure.[1,2] Subsequently, the same authors studied the implications of strong d-f correlation on mixed valence.[3] Throughout the discussion the Ce sites are assumed to be independent of one another. This is a good approximation at high temperatures, but at very low temperatures the sites are known to be correlated, and the elementary excitations are well described by Fermi-liquid theory. This paper attempts to delineate the effects of d-f correlation on the spectrum of the fermion-type quasiparticles in mixed-valence Ce systems.

The model employed here is the single-band spinless model whose Hamiltonian is

$$H = H_0 + V \,, \tag{1}$$

where

$$H_0 = \sum_{\vec{k}} \epsilon_{\vec{k}} d^\dagger_{\vec{k}} d_{\vec{k}} - \epsilon_f \sum_i f_i^\dagger f_i - (U/N) \sum_i \sum_{\vec{k},\vec{k}'} d^\dagger_{\vec{k}} d_{\vec{k}'} f_i f_i^\dagger e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_i} \tag{2}$$

and

$$V = N^{-1/2} \sum_i \sum_{\vec{k}} [V(\vec{k}) d^\dagger_{\vec{k}} f_i e^{-i\vec{k}\cdot\vec{R}_i} + \text{H.c.}] \,. \tag{3}$$

There is one partially filled d band and one nondegenerate f state per Ce atom. The N Ce sites form a periodic lattice. The f levels are normally filled, but when the level on a site is empty, the f hole presents a strong local attraction of strength U to the itinerant d electron. The d-f hybridization is given by the V term. The model is obviously oversimplified, but it is worth studying because it allows some insight into the properties of real mixed-valence Ce systems.

Consider a system in which all N Ce sites are in the f^1 configuration. If we ignore the d-f hybridization, we can construct the ground state of the system,

$$|\psi_1\rangle = \prod_{k<k_F} d^\dagger_{\vec{k}} \prod_i f_i^\dagger |0\rangle \,, \tag{4}$$

where $|0\rangle$ is the vacuum state and k_F is the Fermi momentum. This state satisfies the Schrödinger equation

$$H_0 |\psi_1\rangle = E_1 |\psi_1\rangle \,, \tag{5}$$

with

$$E_1 = \sum_{k<k_F} \epsilon_{\vec{k}} + N\epsilon_f \,. \tag{6}$$

Similarly, we can define a set of excited states $|\psi_n\rangle$ by moving an arbitrary number of d electrons above the Fermi level while keeping all f electrons in place.

When an f hole is created at site i, the d-electron states are modified so that the new eigenstates $|\phi_m(i)\rangle$ are

$$|\phi_m(i)\rangle = \prod_{\{n\}} c_n^\dagger(i) \prod_{j\,(\neq i)} f_j^\dagger |0\rangle \,. \tag{7}$$

The new electron operators $c_n(i)$ are related to the band-electron operators by a canonical transformation,[1,3]

$$c_n(i) = \sum_{\vec{k}} a_{n,\vec{k}} d_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_i} \,, \tag{8}$$

and each state $|\phi_m(i)\rangle$ corresponds to a selected set of occupied one-electron states $\{n\}$. The f-hole states satisfy the Schrödinger equation

$$H_0|\phi_m(i)\rangle=(E'_m-\epsilon_f)|\phi_m(i)\rangle\ , \tag{9}$$

where

$$E'_m=\sum_{\{n\}}\omega_n+N\epsilon_f\ , \tag{10}$$

and the ω_n are the new one-electron energies. A complete set of coherent one-f-hole states can be constructed. These are

$$|\phi_m(\vec{k})\rangle=N^{-1/2}\sum_i|\phi_m(i)\rangle e^{-i\vec{k}\cdot\vec{R}_i}\ , \tag{11}$$

and they satisfy the following orthogonality relation:

$$\langle\phi_{m'}(\vec{k}')|\phi_m(\vec{k})\rangle=\delta_{mm'}\delta_{\vec{k}\,\vec{k}'}\ . \tag{12}$$

The d-f—hybridization interaction in Eq. (3) allows the f^0 site to propagate, and the propagating states constitute the quasiparticles of the system. A complication arises in the calculation because the V term also modifies the ground state. The quasiparticle energy is, by definition, the difference in energy between the ground state and the one-f-hole state. Both energies are $O(N)$, while we are seeking their difference, which is $O(1)$. The d-f interaction precludes the use of Wick's theorem to effect the subtraction analytically. We therefore do the subtraction formally by using the equation-of-motion technique as follows. We denote the true ground state by $|\chi_1\rangle$, the energy of which is $\mathscr{E}_1$, i.e.,

$$H|\chi_1\rangle=\mathscr{E}_1|\chi_1\rangle\ . \tag{13}$$

Let $\alpha_{\vec{k}}$ be the annihilation operator of a quasiparticle the energy of which is $\Omega_{\vec{k}}$; then

$$H\alpha_{\vec{k}}|\chi_1\rangle=(\mathscr{E}_1-\Omega_{\vec{k}})\alpha_{\vec{k}}|\chi_1\rangle\ . \tag{14}$$

We obtain the equation of motion of $\alpha_{\vec{k}}$ by combining the two equations,

$$\Omega_{\vec{k}}\alpha_{\vec{k}}=[\alpha_{\vec{k}},H]\ . \tag{15}$$

Considering the d-electron operator, we find

$$[d_{\vec{k}},H]=[d_{\vec{k}},H_0]+V(\vec{k})f_{\vec{k}}\ ,$$

where

$$f_{\vec{k}}=N^{-1/2}\sum_i f_i e^{-i\vec{k}\cdot\vec{R}_i}\ . \tag{16}$$

Similarly, for the f-electron operator,

$$[f_{\vec{k}},H]=[f_{\vec{k}},H_0]+V^*(\vec{k})d_{\vec{k}}\ .$$

In the above equations the V term mixes $d_{\vec{k}}$ with $f_{\vec{k}}$. The commutators involving H_0 are complicated by the presence of the U term. Consider a lattice in which all sites are f^1. Clearly, the contribution of the U term to $[d_{\vec{k}},H_0]$ is zero. In $[f_{\vec{k}},H_0]$ the U term creates a set of electron-hole pairs on the site where an f electron is removed. We will treat this effect by going to the ϕ states in Eqs. (9) and (11). Therefore, the quasiparticle propagates by changing back and forth between a d hole and an f hole, and the latter carries with it the response of the d-electron system. The calculation is valid when the number of quasiparticles in the system approaches zero.

It is still difficult to solve the equations of motion directly. Since $f_{\vec{k}}$ is only mixed with $d_{\vec{k}}$, we may simplify the problem by truncating the d-f—hybridization interaction to one term:

$$V'=V(\vec{k})d^\dagger_{\vec{k}}f_{\vec{k}}+\text{H.c.} \tag{17}$$

For $k<k_F$ it is easy to see that $V'|\psi_1\rangle=0$. Hence the ground state $|\chi_1\rangle=|\psi_1\rangle$. All other terms in V contribute equally to the ground-state and the one-hole-state energies. As long as the number of quasiparticles in the true ground state is few, the use of $|\psi_1\rangle$ to approximate the ground state should yield a good approximation. The trial wave function for a quasiparticle is taken as

$$|\chi_{\vec{k}}\rangle=|\psi_{\vec{k}}\rangle+\sum_m\lambda_m\phi_m(\vec{k})\ , \tag{18}$$

where $|\psi_{\vec{k}}\rangle=d_{\vec{k}}|\psi_1\rangle$. This state satisfies the Schrödinger equation

$$H'|\chi_{\vec{k}}\rangle=(E_1-\Omega_{\vec{k}})|\chi_{\vec{k}}\rangle\ , \tag{19}$$

with $H'=H_0+V'$. Inserting Eq. (18) into Eq. (19) and making use of the result

$$H_0|\psi_{\vec{k}}\rangle=(E_1-\epsilon_{\vec{k}})|\psi_{\vec{k}}\rangle\ , \tag{20}$$

we obtain

$$(\Omega_{\vec{k}}-\epsilon_{\vec{k}})|\psi_{\vec{k}}\rangle+\sum_m\lambda_m(E'_m-\epsilon_f-E_1+\Omega_{\vec{k}})|\phi_m(\vec{k})\rangle$$
$$=V(\vec{k})f_{\vec{k}}|\psi_1\rangle+V^*(\vec{k})\sum_m\lambda_m d_{\vec{k}}f^\dagger_{\vec{k}}|\phi_m(\vec{k})\rangle\ . \tag{21}$$

The first term on the right-hand side of Eq. (19) is a one-f-hole state and can be expanded in terms of $|\phi_m(\vec{k})\rangle$. The second term is a d-hole state which contains $|\psi_{\vec{k}}\rangle$ as well as its excited states. However, up to order V^2 the excited states can be ignored. Applying $\langle\psi_{\vec{k}}|$ and $\langle\phi_m(\vec{k})|$ in turn to Eq. (19), we obtain

$$\Omega_{\vec{k}}-\epsilon_{\vec{k}}=\sum_m\lambda_m V^*(\vec{k})\langle\psi_1|f^\dagger_{\vec{k}}|\phi_m(\vec{k})\rangle\ ,$$
$$\lambda_m=V(\vec{k})\langle\phi_m(\vec{k})|f_{\vec{k}}|\psi_1\rangle/(E'_m-\epsilon_f-E_1+\Omega_{\vec{k}})\ . \tag{22}$$

The equation for $\Omega_{\vec{k}}$ is deduced from these results,

$$\Omega_{\vec{k}}-\epsilon_{\vec{k}}=V^2\sum_m\frac{|\langle\phi_m(\vec{k})|f_{\vec{k}}|\psi_1\rangle|^2}{\Omega_{\vec{k}}-\epsilon_f-\Delta+(E'_m-E'_1)}\ , \tag{23}$$

where

$$\Delta=E_1-E'_1=\sum_{k<k_F}(\epsilon_{\vec{k}}-\omega_{\vec{k}}) \tag{24}$$

is the d-f—interaction energy defined in Ref. 3, and we have ignored the $\vec{k}$ dependence of the hybridization potential. Since the unperturbed state is a d-hole state, the result applies for $k < k_F$.

The matrix element can be written in terms of real-space operators,

$$\langle \phi_m(\vec{k}) | f_{\vec{k}} | \psi_1 \rangle = N^{-1} \sum_i \langle \phi_m(i) | f_i | \psi_1 \rangle \ . \tag{25}$$

It will be shown in Appendix A that the matrix elements on the right-hand side of Eq. (25) are independent of the site i, and that they are identical to the matrix element in the photoemission spectrum. In fact, if we denote the spectrum by

$$\rho(\epsilon) = \sum_m | \langle \phi_m(i) | f_i | \psi_1 \rangle |^2 \delta(\epsilon - E'_m + E'_1) \ , \tag{26}$$

then Eq. (23) has the simple form

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = V^2 \int_0^\infty \frac{\rho(\epsilon')}{\Omega_{\vec{k}} - \epsilon_f - \Delta + \epsilon'} d\epsilon' \ . \tag{27}$$

The lower limit of the integral is the threshold of the spectrum.

Some analytical properties of the quasiparticles can be inferred readily from Eq. (27). The function $\rho(\epsilon)$ has two peaks, one at $\epsilon_f + \Delta$ and another at a lower energy $\epsilon_f + \Delta - (\mu - \omega_1)$. Consequently, the f level appears at two places, each forming hybridized bands with d electrons. The first one is relevant to the mixed-valence problem because it is situated near the Fermi energy. If the quantity $|\epsilon_{\vec{k}} - \epsilon_f - \Delta|$ is greater than the width of the first peak, but much less than the separation between the two peaks, we can simplify Eq. (27) as

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = V^2 I_1 / (\Omega_{\vec{k}} - \epsilon_f) \ ,$$

where $I_1 = \langle \psi_1 | c_1^\dagger c_1 | \psi_1 \rangle < 1$ is the fractional intensity of the first peak. This shows that the overall width of the first set of hybridized d-f bands is $V(I_1)^{1/2}$. The bands are not narrowed uniformly, however, as can be seen by rewriting Eq. (27) as

$$(\Omega_{\vec{k}} - \epsilon_{\vec{k}})(\Omega_{\vec{k}} - \epsilon_f - \Delta) = V^2 \int_0^\infty \rho(\epsilon') \left[\frac{\Omega_{\vec{k}} - \epsilon_f - \Delta}{\Omega_{\vec{k}} - \epsilon_f - \Delta + \epsilon'} \right] d\epsilon' \ .$$

The right-hand side of the above equation can be looked upon as the square of an energy-dependent d-f—mixing matrix element. The quantity in the large parentheses is less than unity, which again demonstrates the band-narrowing effect. The reduction of the effective matrix element is most pronounced when $\Omega_{\vec{k}} \cong \epsilon_f + \Delta$, i.e., when the quasiparticle is more f-like. Thus, the quasiparticle mass is enhanced over the band mass by two effects, one being the hybridization with f states as in the conventional model, and the other the reduction of effective hybridization strength by d-f correlation. The latter can be tested experimentally by correlating the mass with the photoemission spectrum. Those materials with smaller I_1, i.e., a weaker peak at the Fermi level, should have a higher band mass.

We also see that Eq. (17) has a real root $\Omega_{\vec{k}} > \epsilon_f + \Delta$, which is the upper branch of the first set of hybridized d-f bands. All other branches are inherently damped because the energy $\Omega_{\vec{k}}$ lies within the continuum of the f^0 spectrum.

It is well documented that $\rho(\epsilon)$ has the following asymptotic expression near the threshold:[4–10]

$$\rho(\epsilon) = \begin{cases} A(\epsilon)^{-\alpha}, & \epsilon > 0 \\ 0, & \epsilon < 0 \end{cases} \tag{28}$$

where $\alpha = 1 - (\delta/\pi)^2$, δ is the d-electron phase shift at the Fermi level, $A \cong (1.78\mu)^{\alpha-1}/\Gamma(1-\alpha)$, and ϵ is the binding energy. Then Eq. (23) can be cast in the form

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = V^2 A \int_0^\infty \frac{d\epsilon'}{(\Omega_{\vec{k}} - \epsilon_f - \Delta + \epsilon')(\epsilon')^\alpha} \ . \tag{29}$$

The integral can be carried out explicitly. For the upper branch we obtain

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = \pi V^2 A \csc[\pi(1-\alpha)] (\Omega_{\vec{k}} - \epsilon_f - \Delta)^{-\alpha} \ , \tag{30}$$

and for the lower branch,

$$\epsilon_{\vec{k}} - \Omega_{\vec{k}} = \pi V^2 A \{\cot[\pi(1-\alpha)] - i\} (\epsilon_f + \Delta - \Omega_{\vec{k}})^{-\alpha} \ . \tag{31}$$

The damping of the lower branch is strong near the crossing point of the unmixed bands, $\epsilon_{\vec{k}} \cong \epsilon_f + \Delta$, and diminishes away from this point.

It is of interest to estimate the quasiparticle level width in the lower branch near the crossing point, i.e., $\Omega_{\vec{k}} - \epsilon_f - \Delta \simeq V$. We find from Eqs. (27) and (28) that

$$\mathrm{Im}\Omega_{\vec{k}} = \pi V (1.78\mu/V)^{\alpha-1}/\Gamma(1-\alpha) \simeq V$$

because the multiplicative factor is of the order of unity. We conclude that the level width is comparable to the bandwidth, and consequently the lower branch represents localized excitations as described by the impurity lattice model.[3]

The quasiparticle spectrum for $k > k_F$ must be obtained by considering the excitation of a d electron and an f hole pair from the ground state. For this purpose we need to define a complete set of states $|\bar{\phi}_m(i)\rangle$ which have one more band electron than $|\psi_1\rangle$. Then the ground state $|\chi_1\rangle$ is a mixed state of the form

$$|\chi_1\rangle = |\psi_1\rangle + \sum_m \lambda_m |\bar{\phi}_m(0)\rangle \ , \tag{32}$$

where

$$|\bar{\phi}_m(0)\rangle = N^{-1/2} \sum_i |\bar{\phi}_m(i)\rangle \tag{33}$$

is a coherent f hole of zero wave vector. A completely parallel discussion gives the following equation for the ground-state energy $\mathscr{E}_1$:

$$\mathscr{E}_1 - E_1 = \sum_m \frac{|V(\vec{k})|^2 |\langle \bar{\phi}_m(0)| d^\dagger_{\vec{k}} f_{\vec{k}} |\psi_1\rangle|^2}{\bar{E}'_m - \mathscr{E}_1 - \epsilon_f} , \tag{34}$$

where E' is the energy of $|\bar{\phi}_m(i)\rangle$. We define the quasiparticle energy by

$$\Omega_{\vec{k}} = E_1 - \mathscr{E}_1 + \epsilon_{\vec{k}} . \tag{35}$$

Then Eq. (34) can be rewritten as

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = V^2 \sum_m \frac{|\langle \phi_m(0)| d^\dagger_{\vec{k}} f_{\vec{k}} |\psi_1\rangle|^2}{\Omega_{\vec{k}} - \epsilon_f - \Delta + \mu - \epsilon_{\vec{k}} + \bar{E}'_m - \bar{E}'_1} , \tag{36}$$

where we have made use of the fact that $\bar{E}'_1 = E'_1 + \mu$. Thus, the solution consists of an upper branch of real energies with $\Omega_{\vec{k}} > \epsilon_f + \Delta - \mu + \epsilon_{\vec{k}}$ and a lower branch of complex energies with $\mathrm{Re}\Omega_{\vec{k}} < \epsilon_f + \Delta - \mu + \epsilon_{\vec{k}}$. It will be shown in Appendix A that the matrix element

$$\langle \bar{\phi}_m(0)| d^\dagger_{\vec{k}} f_{\vec{k}} |\psi_1\rangle = \langle \bar{\phi}_m(i)| d^\dagger_{\vec{k}} f_i |\psi_1\rangle e^{-i\vec{k}\cdot\vec{R}_i} , \tag{37}$$

where i is an arbitrary site. The last matrix element is closely related to that for the photoemission spectrum. Away from the band-crossing point the hybridization interaction is reduced by the square root of

$$\langle \psi_1| d_{\vec{k}} c^\dagger_1 c_1 d^\dagger_{\vec{k}} |\psi_1\rangle = I_1 + O(1/N) . \tag{38}$$

In the vicinity of the band-crossing point the equation for $\Omega_{\vec{k}}$ can be reduced to

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = V^2 A \left[\int_0^\infty \frac{d\epsilon'}{(\Omega_{\vec{k}} - \epsilon_f - \Delta + \epsilon')(\epsilon')^\alpha} + \int_{-(\epsilon_{\vec{k}} - \mu)}^\infty \frac{d\epsilon'}{(\Omega_{\vec{k}} - \epsilon_f - \Delta + \epsilon')(-\epsilon')^\alpha} \right] , \tag{39}$$

which is the analytic continuation of Eq. (28) to the region $k > k_F$. Thus, the dispersion relation for $k > k_F$ joins smoothly with that for $k < k_F$.

The coefficients λ_m in Eqs. (16) and (31) measure the amount of f character in the mixed wave function. We denote the f content by x_f, and then

$$x_f = \sum_m |\lambda_m|^2 \Big/ \left[1 + \sum_m |\lambda_m|^2 \right] \tag{40}$$

for all $\vec{k}$. We now derive a very simple relation between x_f and the effective mass of the mixed d-f band. It is readily found from Eq. (23) that

$$\left[\frac{d\Omega_{\vec{k}}}{d\epsilon_{\vec{k}}} \right]^{-1} = 1 + V^2 \sum_m \frac{|\langle \phi_m(\vec{k})| f_{\vec{k}} |\psi_1\rangle|^2}{(\Omega_{\vec{k}} - \epsilon_f - \Delta + E'_m - E'_1)^2}$$

$$= 1 + \sum_m |\lambda_m|^2 . \tag{41}$$

The left-hand side of (41) is equal to m^*/m_0, where m^* is the mass of the mixed d-f band and m_0 is the mass of the d band. It follows from Eq. (40) that

$$m^*/m_0 = 1/(1 - x_f) . \tag{42}$$

The same result is obtained for $k > k_F$. The d-f correlation effects do not appear explicitly in this relation, so it holds regardless of how the correlation effects are treated.

Metallic Ce and many of its intermetallic compounds have $4f$ occupation numbers very close to 1. They also have high densities of states at the Fermi level. Both properties are obtained from our model by placing the Fermi level slightly above $\epsilon_f + \Delta$, i.e., $0 < \mu - (\epsilon_f + \Delta) < V$.

At an elevated temperature the quasiparticle problem must be solved by considering an ensemble of states $|\psi_n\rangle$ which have no f holes and a complete set of states $|\phi_m(\vec{k})\rangle$ which have one f hole. A similar calculation yields

$$\Omega_{\vec{k}} - \epsilon_{\vec{k}} = V^2 \sum_n P_n \sum_{m,\vec{k}'} \frac{|\langle \phi_m(\vec{k}')| f_{\vec{k}} |\psi_n\rangle|^2}{\Omega_{\vec{k}} - \epsilon_f - \Delta + E'_m - \delta E_n} , \tag{43}$$

where

$$P_n = e^{-\beta E_n} \Big/ \sum_n e^{-\beta E_n} ,$$

with $\beta = 1/k_B T$, $\delta E'_m = E'_m - E'_1$, and $\delta E_n = E_n - E_1$. By momentum conservation the matrix element vanishes unless $\vec{k}' + \vec{k}$ is equal to the total momentum of the state $|\psi_n\rangle$. In the latter case,

$$\langle \phi_m(\vec{k}')| f_{\vec{k}} |\psi_n\rangle = \langle \phi_m(i)| f_i |\psi_n\rangle ,$$

and the sum of $\vec{k}'$ is dropped. Again, the result can be written in the form of Eq. (27) with

$$\rho(\epsilon) = \sum_{m,n} P_n |\langle \phi_m(i)| f_i |\psi_n\rangle|^2 \delta(\epsilon - \delta E'_m + \delta E_n) , \tag{44}$$

which is the photoemission spectrum of the f electron at finite temperatures. We will calculate this quantity by using the effective boson model.[11,12]

In the boson model the particle-hole pairs are treated as independent harmonic oscillators. In the f^1 state the Hamiltonian of the harmonic oscillators is

$$H = \sum_i \omega_i a_i^\dagger a_i , \tag{45}$$

where ω_i is the energy and a_i is the annihilation operator of the ith mode. The Hamiltonian of the f^0 state is

$$H' = H + \sum_i \lambda_i (a_i^\dagger + a_i) , \tag{46}$$

where $\{\lambda_i\}$ are the coupling constants. The Hamiltonian H' is diagonalized by the canonical transformation

$$b_i = a_i + \lambda_i/\omega_i \ ,$$

with the result

$$H' = \sum_i \omega_i b_i^\dagger b_i - \sum_i \lambda_i^2/\omega_i \ . \tag{47}$$

The photoemission spectrum from the ground state is the Fourier transform of the following function:

$$f(t) = \exp\left[\sum_i \left[\frac{\lambda_i}{\omega_i}\right]^2 (e^{i\omega_i t} - 1)\right] . \tag{48}$$

The sum over i is transformed into an integral by introducing the density of harmonic-oscillator states $N(\omega)$,

$$\sum_i \left[\frac{\lambda_i}{\omega_i}\right]^2 (e^{-\omega_i t} - 1) = \int_0^{\omega_c} \frac{\lambda^2(\omega) N(\omega)}{\omega^2} (e^{-\omega t} - 1) d\omega \ . \tag{49}$$

The edge singularity is reproduced if we identify the cutoff frequency $\omega_c = \mu$ and the coupling parameter[12]

$$\lambda^2(\omega) N(\omega) = (1-\alpha)\omega \ . \tag{50}$$

At finite temperatures we find that

$$f(t) = \exp\left[(1-\alpha)\int_0^\mu \frac{d\omega}{\omega}\{[n(\omega)-1](e^{-\omega t}-1) + n(\omega)(e^{-i\omega t}-1)\}\right] , \tag{51}$$

where $n(\omega) = (e^{\beta\omega}-1)^{-1}$. The derivation of this result and the subsequent Fourier transformation are given in Appendix B. The result for the spectrum is

$$\rho(\epsilon) = \frac{(1.78\mu)^{\alpha-1}}{2\pi}\left[\frac{\pi}{\beta}\right]^{1-\alpha} \frac{\sin[\pi(1-\alpha)]}{\cosh(\beta\epsilon) - \cos[\pi(1-\alpha)]} \times \int_0^\beta e^{\epsilon\tau}\left|\sin\frac{\pi\tau}{\beta}\right|^{\alpha-1} d\tau \ . \tag{52}$$

The energy ϵ is again the binding energy measured from the threshold. The spectrum is shown in Fig. 1 for a number of temperatures. One outstanding feature is that at nonzero temperature the spectrum is nonzero at the negative-binding-energy side. At low temperatures, $\beta|\epsilon| \gg 1$, we find

$$\rho(\epsilon) \propto \begin{cases} (\epsilon)^{-\alpha}, & \epsilon > 0 \quad (53) \\ e^{-\beta|\epsilon|}\,|\epsilon|^{-\alpha}, & \epsilon < 0 \ . \quad (54) \end{cases}$$

At high temperatures, $\beta|\epsilon| \ll 1$, the spectrum is rather flat and

$$\rho(\epsilon) \propto T^{-\alpha} \ . \tag{55}$$

A direct consequence of the finite $\rho(\epsilon)$ on the negative-ϵ side is that the upper branch of the d-f—hybridized band now acquires a finite level width. We have

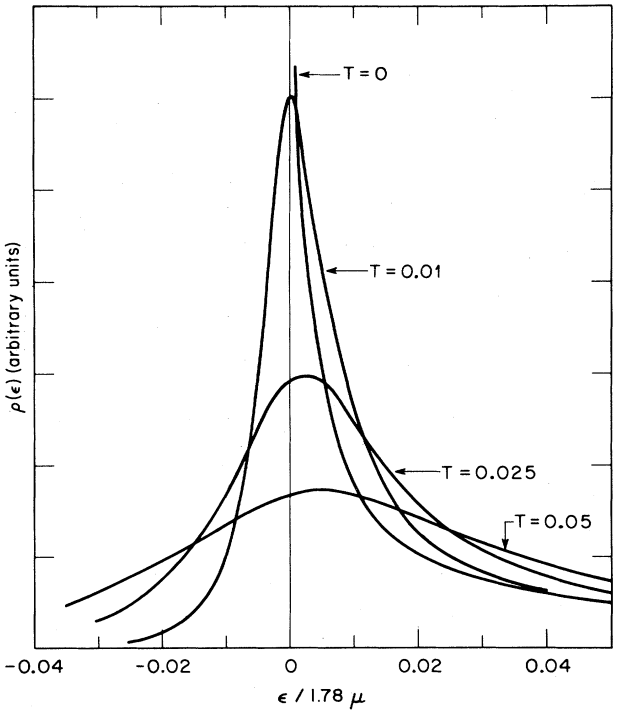

FIG. 1. Temperature dependence of the f-electron photoemission spectrum. The temperature is expressed in units of $e^\gamma\mu/k$, $e^\gamma = 1.78$.

$$\mathrm{Im}\Omega_{\vec{k}} = \pi V^2 \rho(\mathrm{Re}\Omega_{\vec{k}} - \epsilon_f - \Delta) \ .$$

In Fig. 2 we show the temperature dependence of the level width for a number of quasiparticle energies $\epsilon = \mathrm{Re}\Omega_{\vec{k}} - \epsilon_f - \Delta$. If the quasiparticle is at the Fermi level, then its level width is related to the electrical resistivity of the material. The results in Fig. 2 resemble very nicely the observed resistivity curves, except at very low temperatures where the resistivity is determined by scattering of quasiparticles from each other. For the d-f—interaction contribution discussed here, the temperature dependence satisfies a scaling relation

$$R(T) \propto F(\epsilon/k_B T) \ ,$$

where $\epsilon = \mu - \epsilon_f - \Delta$, and

$$F(x) = \frac{x^{\alpha-1}\sin[\pi(1-\alpha)]}{\cosh x - \cos[\pi(1-\alpha)]}\int_0^x e^y \left|\sin\left[\frac{\pi y}{x}\right]\right|^{\alpha-1} dy \ . \tag{56}$$

The scaling relation holds as long as the index α does not vary too much from one material to another. Such a scaling relation is well documented for the magnetic susceptibility of Ce-based mixed-valence materials.[13–15]

At high temperatures the resistivity has the T dependence given in Eq. (55). This result was predicted on the basis of the impurity model.[3] Thus, the present theory describes in a natural way the deterioration of f-site correla-

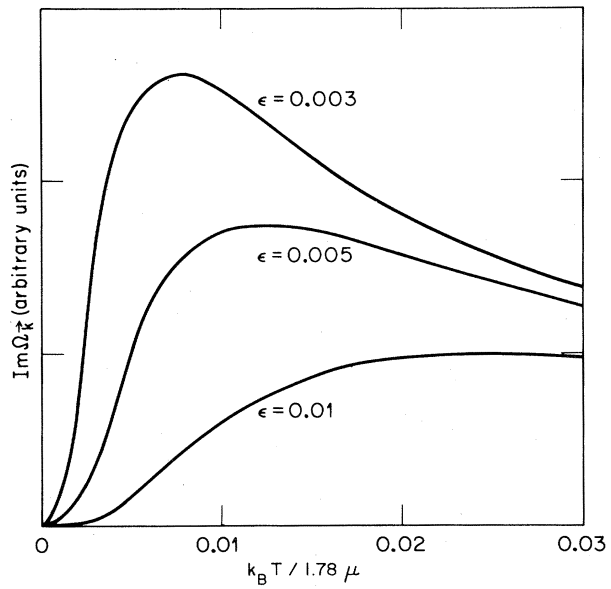

FIG. 2. Temperature dependence of the level width of quasiparticles in the upper branch of the mixed d-f band. The quantity $\epsilon=\Omega_{\vec{k}}-\epsilon_f-\Delta$, in units of 1.78μ, is the quasiparticle energy measured from the edge singularity at $\epsilon_f+\Delta$. The same curves represent the temperature dependence of the resistivity if ϵ is the Fermi level measured from the singularity.

tion at elevated temperatures.

In summary, we have studied the effects of strong d-f correlation on the quasiparticle spectrum of a mixed-valence system in the approximation that all sites have f^1 configuration. A new mechanism of mass enhancement has been found, and experimental verification has been proposed. At finite temperatures the quasiparticle band naturally deteriorates into incoherent local excitations, and this gives rise to an electrical resisistivity whose temperature dependence satisfies a simple scaling relation.

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APPENDIX A: MATRIX ELEMENTS

The properties of the d-f—mixing matrix elements in Eqs. (23) and (35) are investigated here. Consider an f hole at site i. The relevant part of H_0 is

$$H_0=\sum_{\vec{k}}\epsilon_{\vec{k}}d^{\dagger}_{\vec{k}}d_{\vec{k}}-(U/N)\sum_{\vec{k},\vec{k}'}d^{\dagger}_{\vec{k}}d_{\vec{k}'}e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_i}\ . \tag{A1}$$

This is diagonalized by the transformation in Eq. (8) with[3,10]

$$a_{n,\vec{k}}=A_n/(\epsilon_{\vec{k}}-\omega_n)\ , \tag{A2}$$

where ω_n is a root of the equation

$$1=(U/N)\sum_{\vec{k}}(\epsilon_{\vec{k}}-\omega_n)^{-1}\ , \tag{A3}$$

and A_n is a normalization constant given by

$$A_n^{-2}=\sum_{\vec{k}}(\epsilon_{\vec{k}}-\omega_n)^{-2}\ . \tag{A4}$$

If we approximate the band states by a dense set of evenly spaced nondegenerate levels, we find a one-to-one correspondence between the band states and the new states, i.e.,

$$\omega_{\vec{k}}=\epsilon_{\vec{k}}-(W/\pi N)\delta_{\vec{k}}\ , \tag{A5}$$

where W is the bandwidth and $\delta_{\vec{k}}$ is the phase shift of the band electron in state $\vec{k}$ when scattered by U.[10] The normalization constant is found to be

$$A_n=(W/\pi N)\sin\delta_n\ . \tag{A6}$$

The ground state of the one-f-hole configuration is

$$|\phi_1(i)\rangle=\prod_{\omega_n<\mu}c_n^{\dagger}(i)\prod_{j(\neq i)}f_j^{\dagger}|0\rangle\ . \tag{A7}$$

The matrix element $\langle\phi_1(i)|f_i|\psi_1\rangle$ has the closed expression[8,9]

$$\langle\phi_1(i)|f_i|\psi_1\rangle=\prod_{\epsilon_n<\mu}\frac{\sin\delta_n}{\delta_n}\prod_{\substack{\epsilon_n<\mu,\\ \epsilon_n>\epsilon_m}}\frac{(\epsilon_n-\epsilon_m)(\omega_n-\omega_m)}{(\omega_n-\epsilon_m)(\epsilon_n-\omega_m)}\exp\left[i\sum_n\vec{k}_n\cdot\vec{R}_i\right]\ . \tag{A8}$$

The sum on $\vec{k}_n$ is over all occupied states of $|\psi_1\rangle$, so it is equal to zero on account of the inversion symmetry of the ground state $|\psi_1\rangle$. Further inspection reveals that the exponential factor is equal to 1, independent of the occupation of the ω_n levels. Consequently, all matrix elements $\langle\phi_1(i)|f_i|\psi_1\rangle$ are independent of the site i. The single-site matrix elements are identical to those which appear in the photoemission spectrum.[3,9]

We now turn to the matrix elements in Eq. (36). Consider a state

$$|\bar{\phi}_{\vec{k}}(i)\rangle=c^{\dagger}_{\vec{k}}(i)|\phi_1(i)\rangle\ , \tag{A9}$$

where the one-electron state $c^{\dagger}_{\vec{k}}(i)$ is the one corresponding to the state $\vec{k}$. Using the method outlined in Refs. 8 and 9 we deduce

$$\langle \phi_{\vec{k}}(i) \mid d^{\dagger}_{\vec{k}} f_i \mid \psi_1 \rangle e^{-i\vec{k}\cdot\vec{R}_i} = \langle \phi_1(i) \mid f_1 \mid \psi_1 \rangle \frac{\sin\delta_{\vec{k}}}{\delta_{\vec{k}}} \prod_{\epsilon_n<\mu} \frac{(\epsilon_{\vec{k}}-\epsilon_n)(\omega_{\vec{k}}-\omega_n)}{(\epsilon_{\vec{k}}-\omega_n)(\omega_{\vec{k}}-\epsilon_n)} \exp\left[i \sum_n \vec{k}_n \cdot \vec{R}_i \right] . \tag{A10}$$

The exponential factor reduces to 1 for the same reason as in Eq. (A8), so the matrix element is independent of the site. By the same argument as used previously, we conclude that matrix elements of this form involving all $|\bar{\phi}_m(i)\rangle$ are independent of the site.

Finally, consider a state $|\bar{\phi}_m(i)\rangle$ defined by

$$|\bar{\phi}_m(i)\rangle = c^{\dagger}_m(i) \mid \phi_1(i)\rangle . \tag{A11}$$

The matrix element of this state can be related to the one in Eq. (A10),

$$\langle \bar{\phi}_m(i) \mid d^{\dagger}_{\vec{k}} f_i \mid \psi_1 \rangle = \langle \bar{\phi}_{\vec{k}} \mid d^{\dagger}_{\vec{k}} f_i \mid \psi_1 \rangle \frac{(W/\pi N)\sin\delta_{\vec{k}}}{\epsilon_{\vec{k}}-\omega_n} \times \prod_{\epsilon_n<\mu} \frac{(\omega_m-\omega_n)(\omega_{\vec{k}}-\epsilon_n)}{(\omega_\pi-\epsilon_n)(\omega_{\vec{k}}-\omega_n)} . \tag{A12}$$

In the limit of large N, the product term can be approximated by $\exp[D(\omega_m)-D(\omega_{\vec{k}})]$, where

$$D(\omega) = \frac{1}{\pi} \int_{-\infty}^{\mu} \frac{\delta(\epsilon')d\epsilon'}{\omega-\epsilon'} . \tag{A13}$$

The same mathematical procedure in Ref. 9 leads to the result in Eq. (28).

APPENDIX B: PHOTOEMISSION SPECTRUM AT FINITE TEMPERATURES

Consider one harmonic oscillator. In the f^1 state the oscillator has the eigenstates

$$|\alpha_n\rangle = (n!)^{-1/2}(a^{\dagger})^n \mid \alpha_0\rangle , \tag{B1}$$

where the ground state is defined by

$$a \mid \alpha_0\rangle = 0 . \tag{B2}$$

In the f^0 state the eigenstates are

$$|\beta_n\rangle = (n!)^{-1/2}(b^{\dagger})^n \mid \beta_0\rangle , \tag{B3}$$

where $b = a + \lambda/\omega$, and the new ground state satisfies

$$b \mid \beta_0\rangle = 0 . \tag{B4}$$

The solution of Eq. (B4) is, up to the lowest significant order of λ/ω,

$$|\beta_0\rangle = (1-\lambda^2/2\omega^2) \mid \alpha_0\rangle - (\lambda/\omega) \mid \alpha_1\rangle . \tag{B5}$$

By using Eqs. (B3) and (B5) we deduce that, again to the lowest order of the coupling constant,

$$|\beta_n\rangle = [1-(n+\tfrac{1}{2})(\lambda/\omega)^2] \mid \alpha_n\rangle - (n)^{1/2}(\lambda/\omega) \mid \alpha_{n-1}\rangle - (n+1)^{1/2}(\lambda/\omega) \mid \alpha_{n+1}\rangle . \tag{B6}$$

The contribution of the state $|\alpha_n\rangle$ to the f-electron spectrum is

$$\rho_n(\epsilon) = |\langle \beta_n \mid \alpha_n\rangle|^2 \delta(\epsilon) + |\langle \beta_{n+1} \mid \alpha_n\rangle|^2 \delta(\epsilon-\omega) + |\langle \beta_{n-1} \mid \alpha_n\rangle|^2 \delta(\epsilon+\omega) = 1 + (\lambda/\omega)^2[(n+1)\delta(\epsilon-\omega) + n\delta(\epsilon+\omega) - (2n+1)\delta(\epsilon)] . \tag{B7}$$

This is averaged over the equilibrium ensemble of states and Fourier-transformed to the time domain to obtain

$$f(t) = 1 + (\lambda/\omega)^2[(e^{i\omega t}-1)(\langle n\rangle+1) + (e^{-i\omega t}-1)\langle n\rangle] \simeq \exp\{(\lambda/\omega)^2[(e^{i\omega t}-1)(\langle n\rangle+1) + (e^{-i\omega t}-1)\langle n\rangle]\} . \tag{B8}$$

The total contribution of all harmonic oscillators is obtained by multiplying the individual contributions. The result is in Eq. (51).

After expanding the boson distribution function in powers of $e^{-\beta\omega}$, we evaluate the integral in the exponent of $f(t)$ term by term to obtain

$$\int_0^{\mu} \frac{d\omega}{\omega}(e^{i\omega t}-1) + \sum_{l=1}^{\infty} \int_0^{\mu} \frac{d\omega}{\omega}(e^{-(\beta l+it)\omega} + e^{-(\beta l-it)\omega} - 2e^{-\beta l\omega}) = -\ln(e^{\gamma}\mu) - \ln(\delta - it) - \sum_{l=1}^{\infty} \ln(1+t^2/\beta^2 l^2) , \tag{B9}$$

where $\delta=0^{\dagger}$, γ is the Euler constant, and $e^{\gamma}=1.78$. The function $f(t)$ has the compact expression

$$f(t)=(e^{\gamma}\mu)^{\alpha-1}(\delta-it)^{\alpha-1}\left[\frac{\sinh(\pi t/\beta)}{\pi t/\beta}\right]^{\alpha-1}. \quad \text{(B10)}$$

The spectrum $\rho(\epsilon)$ is the Fourier transform

$$\rho(\epsilon)=\frac{1}{2\pi}\int_{-\infty}^{\infty}f(t)e^{-i\epsilon t}dt\ . \quad \text{(B11)}$$

We use the contour method to evaluate this integral. For $\epsilon>0$ we close the contour by an infinite semicircle below the real axis. The integrand is analytic except for an infinite set of branch cuts along the imaginary axis. The end points of the cuts are $t=-i\delta$ and $t=-in\beta$, $n=1,2,3,\ldots$. The contour is then deformed to wrap around the lower part of the imaginary axis as shown in Fig. 3. Between the end point $-in\beta$ and $-i(n+1)\beta$, the integrand is a real function multiplied by a phase factor $e^{-i(n+1)\pi(1-\alpha)}$ on the right-hand side of the branch cut, and on the left-hand side the phase factor is the complex conjugate. This discontinuity across the branch cut gives the contribution to the contour integral between these two end points. The sum of these contributions is

$$\rho(\epsilon)=\frac{1}{\pi}(e^{\gamma}\mu)^{\alpha-1}\left[\frac{\pi}{\beta}\right]^{1-\alpha}\times\sum_{n=0}^{\infty}\sin[(n+1)\pi(1-\alpha)]\times\int_{n\beta}^{(n+1)\beta}e^{-\epsilon\tau}|\sin(\pi\tau/\beta)|^{\alpha-1}d\tau\ . \quad \text{(B12)}$$

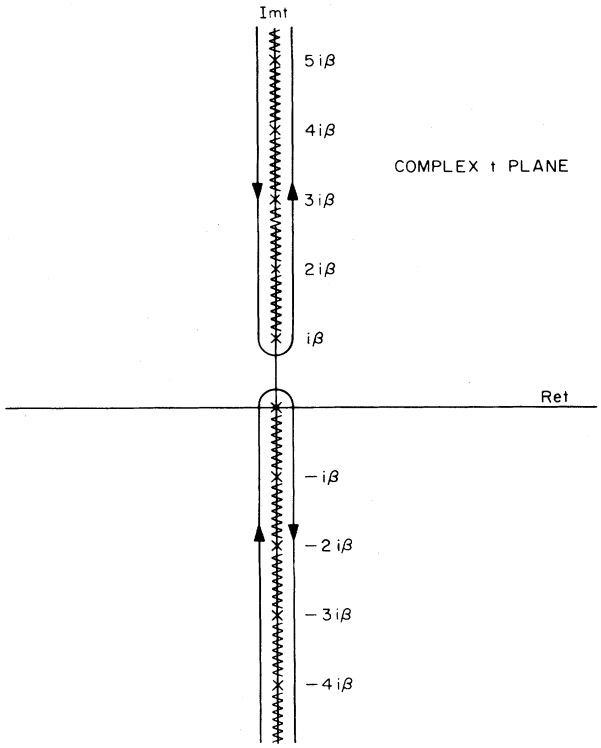

FIG. 3. Contours for the integral in Eq. (B11). The upper contour is for $\epsilon<0$ and the lower one is for $\epsilon>0$.

A few elementary manipulations put the above result in the form of Eq. (52). For $\epsilon<0$ we wrap the contour around the upper half of the imaginary axis and repeat the procedure. The same result is obtained for $\rho(\epsilon)$.

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