

Effects of d - f correlation on the mixed-valent properties of Ce systems

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In a recent paper it was suggested that the double-peak $4f$ photoemission spectra of Ce and $\text{Ce}_{0.9}\text{Th}_{0.1}$ indicate strong d - f correlation. This paper discusses the effects of this correlation on the mixed-valent properties of Ce systems. In the impurity-lattice approximation, which is valid at high temperatures, the f -electron spectrum has the well-known x-ray-edge singularity at the Fermi level. The inclusion of d - f hybridization adds fine structures to the spectrum near the Fermi level. Furthermore, the singularity can account for the Kondo-type resistivity and specific-heat anomalies without the need to invoke spin-flip scattering.

I. INTRODUCTION

The mixed-valent properties of Ce metal and its alloys and intermetallic compounds have been studied exhaustively in recent years. The problem originates from attempts to understand the first-order phase transition from γ -Ce to α -Ce. Both phases have the cubic-closed-packed structure, but on going from the γ phase to the α phase the lattice parameter shrinks by about 6%.¹ The electronic and magnetic properties of Ce are no less intriguing. Both phases have large electronic specific-heat coefficients, which indicate high densities of electron states at the Fermi level. The magnetic susceptibility of γ -Ce follows a Curie-Weiss law with a magnetic moment corresponding to one $4f$ electron per atom. On the other hand, α -Ce has a high but temperature-insensitive susceptibility, which is indicative of a narrow band of electrons.

To explain the γ - α phase change Zachariassen and Pauling² suggested that the volume collapse is caused by the promotion of $4f$ electrons into the conduction band, i.e., the α phase is tetravalent. The added band electron strengthens the metallic bonding and reduces the interatomic distances. This so-called promotion model was carefully analyzed by Ramirez and Falicov,³ who showed that the thermodynamic properties of the phase transition can be understood if the $4f$ level is close to the Fermi level.

Johansson argued against the promotion model by pointing out that α -Ce has a melting temperature (940 K) characteristic of trivalent metals, rather than tetravalent metals (2000 K).⁴ Based on this observation he proposed a band model such that in α -Ce the $4f$ level broadens into a band and that the $4f$ electrons can participate in crystal bonding. There should be no significant difference in $4f$ occupation between the two phases, as confirmed by a number of recent experiments.⁵⁻⁷ Since a $4f$ band has a high degree of degeneracy, the requirement of one $4f$ electron per Ce atom puts the Fermi level near the bottom of the f band. The overlap between nearest-neighbor $4f$

wave functions is insignificant, so the f bandwidth must come from hybridization of $4f$ and conduction-band states. In γ -Ce, however, the $4f$ electrons are in localized states and do not participate in bonding. The electronic and magnetic properties can be reconciled with the picture that the $4f$ states have an intrinsic width due to hybridization.^{8,9} Incidentally, when d - f hybridization is included in the promotion model, the predicted change of f occupation is much reduced, and the model converges to the band model.^{10,11}

The success of the f -band model has stimulated *ab initio* band-structure calculations of both phases of Ce and some Ce intermetallic compounds. Glötzel¹² carried out self-consistent band calculations using the local-density-functional approximation for the crystal potential. He obtained a nonmagnetic $4f$ -band state for α -Ce, but a magnetic ground state with nearly one f electron per atom for γ -Ce. Koelling¹³ has been able to map out the Fermi surface of CeSn_3 and to explain the observed de Haas-van Alphen frequencies of this mixed-valent compound.¹⁴ On the negative side, the band-structure calculation consistently underestimates the effective mass of the band electrons, or equivalently the density of electron states. This suggests that certain many-body correlation effects are present but are not adequately treated by the local-density approximation for the exchange-correlation potential.

A clue to the missing correlation effect has been furnished recently by photoemission experiments.^{15,16} The purpose of the experiments was to verify the theoretical prediction that the $4f$ level should be very near the Fermi level. However, early experiments placed the $4f$ level at around 2–3 eV below the Fermi level for a number of Ce systems.^{17,18} With improved sample-handling technique and the high resolution of synchrotron-radiation sources new and finer measurements have become possible. The resulting $4f$ spectra for both γ - and α -Ce exhibit two peaks, one at the Fermi level and another at 2 eV below. None of the existing models explains adequately the origin

of the double-peak spectrum. In a recent paper the present authors suggested that the unusual structure of the photoemission spectrum of Ce arises from strong d - f correlation.¹⁹ When an f electron is excited out of an atom, the d electrons around that atom experience a large change in local environment such that a localized impurity state is formed. In the final state the impurity state may or may not be occupied, and this gives rise to two peaks in the f -electron spectrum. The separation between the two peaks is equal to the energy of the impurity state measured from the Fermi level.

$$H = \sum_{n, \vec{k}, \sigma} \epsilon_{n\vec{k}} d_{n\vec{k}\sigma}^\dagger d_{n\vec{k}\sigma} + \epsilon_f \sum_{i, \sigma} f_{i\sigma}^\dagger f_{i\sigma} + U_{ff} \sum_i f_{i\sigma}^\dagger f_{i\sigma} f_{i, -\sigma}^\dagger f_{i, -\sigma} - \left(\frac{1}{N} \right) \sum_i \sum_{n, \vec{k}; n', \vec{k}'} \sum_{\sigma, \sigma'} U_{\sigma\sigma'} d_{n\vec{k}\sigma}^\dagger d_{n'\vec{k}'\sigma'} f_{i\sigma}^\dagger f_{i\sigma'} e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_i} + (N)^{-1/2} \sum_i \sum_{n, \vec{k}, \sigma} [V_n(k) f_{i\sigma}^\dagger d_{n\vec{k}\sigma} e^{i\vec{k} \cdot \vec{R}_i} + \text{H.c.}], \quad (2.1)$$

where $d_{n\vec{k}\sigma}$ is the band-electron operator in band n , wave vector \vec{k} , and spin σ , $\epsilon_{n\vec{k}}$ is the band energy, $f_{i\sigma}$ is the f -electron operator for the i th site at \vec{R}_i , ϵ_f is the single-particle energy of the f level, and N is the total number of Ce sites. The d - f interaction term is written in the form of an attraction between a d electron and an f hole. The strengths of the interaction parameter are $U_{ff} \cong 8$ eV,²⁰ which has the effect of preventing multiple occupation of the f orbital, $U \cong 3$ eV,¹⁹ the d - f interaction, and $|V_n(\vec{k})| \cong 0.2$ eV,²¹ the hybridization energy between d and f electrons. Ramirez and Falicov³ first pointed out the importance of the d - f interaction in the α - γ phase transition in Ce, while Kaplan and Mahanti²² invoked this interaction in their theory of the phase transition in SmS. It is customary to treat this term in the mean-field approximation. In this approximation the interaction renormalizes the single-particle energies ϵ_f and $\epsilon_{n\vec{k}}$. Then the hybridization term can be exactly diagonalized to give the mixed d and f bands.

The d - f interaction strength U is comparable to the width of the d band, which is $W \cong 4$ eV.²¹ This fact makes the mean-field approximation questionable. In our approach we treat the U term exactly to the extent possible and handle the hybridization term by perturbation. We will simplify the model somewhat without affecting its physical content. We retain only one band and assume a constant density of states for the band. Since the f level can only be singly occupied, we suppress the spin index, ignore the U_{ff} term, and build the single occupancy into the wave function. We consider as a start the promotion of an f electron from a Ce site into the conduction band. The hybridization is neglected for the moment. Thus the Hamiltonian is reduced to

$$H_0 = \epsilon_f f^\dagger f + \sum_{\vec{k}} \epsilon_{\vec{k}} d_{\vec{k}}^\dagger d_{\vec{k}} - (U/N) \sum_{\vec{k}, \vec{k}'} d_{\vec{k}}^\dagger d_{\vec{k}'} f f^\dagger, \quad (2.2)$$

The origin of the strong d - f correlation is not clear at present. In this paper we start from the assumption that such a strong local interaction exists and proceed to explore its consequences. We will discuss in particular the effects of d - f correlation and d - f hybridization on the photoemission spectrum, the resistivity and the specific heat in the impurity-lattice approximation.

II. SINGLE-SITE PROBLEM

The important interactions in a mixed-valent metal are embodied in the following model Hamiltonian:

where the selected Ce site is at the origin. The eigenstates of the system can be solved exactly for both f^0 and f^1 configurations.²³ In the f^1 configuration the ground state is $f^\dagger |\Psi_1\rangle$, where

$$|\Psi_1\rangle = \prod_{\vec{k}} d_{\vec{k}}^\dagger |0\rangle, \quad (2.3)$$

$|0\rangle$ is the vacuum state, and N_e is the number of band electrons. The ground-state energy is

$$E_1 = \epsilon_f + \sum_{\vec{k}} \epsilon_{\vec{k}}. \quad (2.4)$$

In the f^0 configuration the Hamiltonian is diagonalized by a canonical transformation

$$c_n = \sum_{\vec{k}} a_{n\vec{k}} d_{\vec{k}}, \quad (2.5)$$

such that

$$H_0 = \sum_n \omega_n c_n^\dagger c_n. \quad (2.6)$$

The new energy levels ω_n are solved from the equation

$$1 = (U/N) \sum_{\vec{k}} (\epsilon_{\vec{k}} - \omega_n)^{-1}. \quad (2.7)$$

There is a one-to-one correspondence between the new states labeled by n and the old states labeled by \vec{k} . The lowest level ω_1 falls below the band to form an impurity level. Measured from the bottom of the band we have

$$\omega_1 = -W / [\exp(W/U) - 1]. \quad (2.8)$$

The levels in the continuum are each shifted by an infinitesimal amount. Under the assumption of uniformly distributed levels in $0 \leq \epsilon_n \leq W$, the n th level ($2 \leq n \leq N$) is

$$\omega_n = \epsilon_n - W \delta_n / N \pi, \quad (2.9)$$

where ϵ_n is the energy of the n th band level and δ_n is the scattering phase shift

$$\delta_n = \tan^{-1} \left[\pi \left[\frac{W}{U} + \ln \frac{\epsilon_n}{W - \epsilon_n} \right]^{-1} \right]. \quad (2.10)$$

The eigenstates of the system are

$$|\phi_i\rangle = \prod_n c_n^\dagger |0\rangle, \quad (2.11)$$

with energies

$$E_i = \sum_n \omega_n, \quad (2.12)$$

where the index n runs over $N_e + 1$ electrons. In particular the ground-state energy is

$$E_1' = \sum_{n=1}^{N_e+1} \omega_n. \quad (2.13)$$

We compare the ground-state energies of the two configurations

$$E_1 - E_1' = \epsilon_f - \omega_{N_e+1} + \sum_{n=1}^{N_e} (\epsilon_n - \omega_n).$$

We identify the last filled level ω_{N_e+1} with the Fermi energy μ and define the d - f interaction energy by²⁴

$$\Delta = \sum_{n=1}^{N_e} (\epsilon_n - \omega_n) = (W/N\pi) \sum_{n=1}^{N_e} \delta_n. \quad (2.14)$$

Then we can write

$$E_1 = E_1' = \epsilon_f + \Delta - \mu. \quad (2.15)$$

The f^1 state becomes unstable if $E_1 - E_1' \geq 0$, i.e., if $\mu - \epsilon_f \leq \Delta$.²⁵ Thus if Δ is sufficiently large, the system tends to convert f^1 sites into f^0 sites even though the single-particle energy ϵ_f is below the Fermi level.

With every additional f electron promoted into the band, the Fermi energy increases by the amount $\delta\mu = W/N$. According to Eq. (2.9) the d - f interaction energy increases by

$$\delta\Delta = \left[\frac{W}{N\pi} \right] \tan^{-1} \left[\pi \left[\frac{W}{U} + \ln \frac{\mu}{W - \mu} \right]^{-1} \right] \leq \delta\mu. \quad (2.16)$$

Consequently, the system gains decreasing amount of energy with increasing number of f^0 sites. Under suitable conditions the promotion process stops after a fraction of sites are converted to f^0 . When this happens the system is mixed valent. We can find the number of f^0 sites at equilibrium by the following consideration. Treating the system as a set of independent Ce sites, we find that the total energy with N_0 sites in f^0 and $N - N_0$ sites in f^1 is

$$E = (N - N_0)\epsilon_f + \sum_k^{N_e+N_0} \epsilon_k - N_0\Delta(N_e + N_0), \quad (2.17)$$

where $\Delta(N')$ is the d - f interaction energy of a single site when the number of band electrons is N' . The equilibri-

um condition as determined by $dE/dN_0 = 0$ is

$$\mu(N_e + N_0) = \epsilon_f + \Delta(N_e + N_0) + N_0(d\Delta/dN_0), \quad (2.18)$$

where the left-hand side is the Fermi energy of the mixed-valent state. The quantity N_0 is solved from this implicit equation. The equilibrium condition also means that the energy required to create or destroy an f^0 site is zero. Or equivalently, the Fermi level is pinned to the fully relaxed f -level energy given by the right-hand side of Eq. (2.18). The last term in Eq. (2.18) comes from relaxation of the number of f^0 sites.

In this discussion we have treated the crystal as a collection of noninteracting Ce sites. The feasibility of this approximation is considered in the Appendix in which we solve the problem of two f^0 sites in a lattice of f^1 sites. It is shown that the two sites repel one another with a short-range potential such that their interaction energy is negligible when they are three or more lattice spacings apart. Thus the approximation is valid as long as the number of promoted sites is low, which is believed to be the case for both phases of Ce.

We calculate the f -electron spectrum through the retarded propagator defined by

$$G(t) = -i \langle [f(t), f^\dagger(0)] \rangle \Theta(t), \quad (2.19)$$

where $f(t)$ is the Heisenberg operator

$$f(t) = e^{iHt} f e^{-iHt}, \quad (2.20)$$

and H is defined in Eq. (2.2). The square bracket denotes the anticommutator between two Heisenberg operators; the expectation value is taken in the ground state of the system; $\Theta(t) = 1$ for $t > 0$ and $\Theta(t) = 0$ otherwise. The Fourier transform of $G(t)$ is

$$G(\nu) = \int_0^\infty G(t) e^{-i\nu t} dt, \quad (2.21)$$

and the spectral density is given by

$$\rho_f(\nu) = -(1/\pi) \text{Im} G(\nu). \quad (2.22)$$

If the site is in the f^1 configuration, we calculate the spectral density by inserting a complete set of f^0 states. We write

$$G(t) = -i \sum_m \langle \phi_m | f | \psi_1 \rangle | \phi_m \rangle^2 e^{i(E_1 - E_m')t}. \quad (2.23)$$

The spectral density calculated from Eq. (2.23) is

$$\rho_f(\nu) = \sum_m \langle \phi_m | f | \psi_1 \rangle | \phi_m \rangle^2 \delta(\nu - E_1 + E_m'). \quad (2.24)$$

In photoemission experiments the binding energy is to be identified with $-\nu$. As discussed in Ref. 19 the spectrum has two peaks; one appears at $\nu_1 = E_1 - E_1'$, and the other appears at $\nu_2 = \nu_1 - \mu + \omega_1$. The singular nature of the peaks has been discussed by many authors.²⁶⁻³¹ The problem is identical to that of the x-ray-absorption edge. The spectrum has the analytic form

$$\rho_f(\nu) \propto (\nu_1 - \nu)^{-\Delta} \quad (2.25)$$

for $\nu \leq \nu_1$, where $\Delta = 1 - (\delta/\pi)^2$, and δ is the scattering phase shift at the Fermi level given by putting $\epsilon_n = \mu$ in

Eq. (2.16). In a strongly interacting system $U/W \cong 1$, one finds $\delta \cong \pi/2$ and $\Delta \cong 0.75$ for a range of μ near the middle of the band. The spectrum is also singular at ν_2 , but this singularity is broadened by lifetime effects. The spectrum of an f^0 site is calculated in an analogous way, with the result

$$\rho'_f(\nu) = \sum_m |\langle \phi_1 | f | \psi_m \rangle|^2 \delta(\nu - E_m + E'_1), \quad (2.26)$$

where $|\psi_m\rangle$ are excited states of $|\psi_1\rangle$ with energy E_m . This spectrum is restricted in the energy range $\nu > \nu_1$, and has one peak at ν_1 having the same singular analytic property as the ν_1 peak of $\rho_f(\nu)$. The total spectral density given by

$$\rho_f^{\text{tot}}(\nu) = (1 - N_0/N)\rho_f(\nu) + (N_0/N)\rho'_f(\nu) \quad (2.27)$$

is sketched in Fig. 1. As discussed earlier the Fermi level is so situated that the energy required to promote the next f electron to the Fermi level is zero. This means that the peak ν_1 appears at the Fermi energy μ and the lower peak ν_2 appears at ω_1 .

III. EFFECTS OF d - f HYBRIDIZATION

We now discuss the effects of adding the hybridization term to the Hamiltonian H of the one-site problem as follows:

$$H_1 = H_0 + N^{-1/2} \sum_{\vec{k}} [V(k) f^\dagger d_{\vec{k}} + \text{H.c.}] \quad (3.1)$$

The last term mixes the many-body states of f^1 and f^0 configurations. Consider the single-site problem with the ground state in the f^1 configuration. We can calculate the perturbed energy of this state by using the standard many-body perturbation method. The equation of the new energy \bar{E}_1 is found to be

$$\bar{E}_1 = E_1 + V^2 \sum_i |M_{1i}|^2 / (\bar{E}_1 - E'_i), \quad (3.2)$$

where V is an average of $V(k)$ at the Fermi energy and the matrix element

$$M_{1i} = N^{-1/2} \sum_{\vec{k}} \langle \psi_1 | d_{\vec{k}} | \phi_i \rangle. \quad (3.3)$$

The last term on the right-hand side of Eq. (3.2) is the lowest-order self-energy of an f electron due to d - f hybridization. The matrix element is the same as that for x-ray absorption by exciting a core electron in a metal.²⁶⁻³¹ The matrix element has the singular behavior

$$|M_{1i}|^2 = A (E'_i - E'_1)^{-\Delta'}, \quad (3.4)$$

where

$$\Delta' = \frac{2\delta}{\pi} - (\delta/\pi)^2, \quad (3.5)$$

and the constant A can be evaluated. In the strong interaction case $U/W \cong 1$, we find $\delta \cong \pi/2$ and $\Delta' \cong 0.75$. The sum in Eq. (3.2) can be converted into an integral and evaluated in closed form. The equation for \bar{E}_1 is found to be

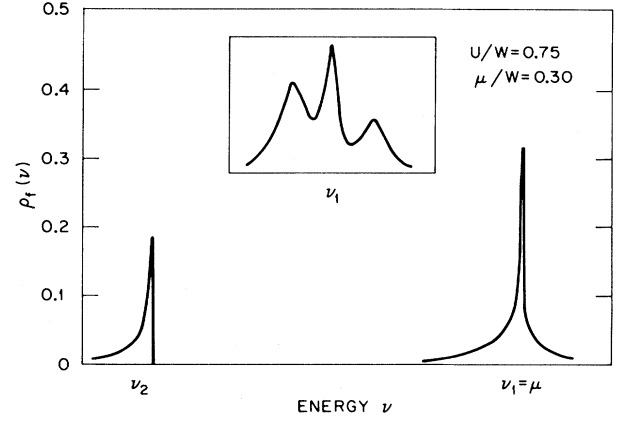


FIG. 1. Spectral density of the f electron in the one-site approximation. Inset shows the fine structure near the Fermi level due to d - f hybridization.

$$\bar{E}_1 - E_1 = -V^2 A \pi \csc[\pi(1 - \Delta')](E'_1 - \bar{E}_1)^{-\Delta'}. \quad (3.6)$$

The perturbed ground-state energy is shifted down from E_1 . In the case of $V \gg E'_1 - E_1$ the energy shift is scaled by $V^{2/(1+\Delta')}$.

The ground-state wave function is given by

$$|\chi_1\rangle = f^\dagger |\psi_1\rangle + V \sum_i \frac{|M_{1i}|}{\bar{E}_1 - E'_i} |\phi_i\rangle, \quad (3.7)$$

which is a bonding linear combination of f^1 and f^0 states. The f content of this wave function is less than one. Thus with the help of d - f hybridization fractional valence becomes possible even when the unperturbed ground-state energy E'_1 of f^0 is higher than E_1 of f^1 as long as $E'_1 - E_1$ is of the same order of magnitude as V .

In a similar manner we find that the perturbed energy of the lowest f^0 state is solved from

$$\begin{aligned} \bar{E}'_1 &= E'_1 + V^2 \sum_i |M_{i1}|^2 / (\bar{E}'_1 - E_i) \\ &= E'_1 + \pi V^2 A \{ \cot[\pi(1 - \Delta')] + i \} (\bar{E}'_1 - E_1)^{-\Delta'}. \end{aligned} \quad (3.8)$$

The energy is complex because this level lies in the continuum of f^1 states. The wave function of this state is

$$|\chi'_1\rangle = |\phi_1\rangle + V \sum_i \frac{|M_{i1}|}{\bar{E}'_1 - E_i} f^\dagger |\psi_i\rangle, \quad (3.9)$$

which is the antibonding linear combination of f^1 and f^0 states.

The same consideration applies to the excited states. The entire level scheme consists of a set of bonding orbitals with energies \bar{E}_i and wave functions χ_i and antibonding orbitals with energies \bar{E}'_i and wave function χ'_i . The low-lying excited states have real energies and all have the impurity level ω_1 filled. For a lattice of independent Ce sites, one finds that every site is a mixture of f^1 and f^0 configurations, and the amount of mixing is the same for

every site.

The photoemission spectrum can be calculated in the same manner as in Sec. II. The ground state is χ_1 in Eq. (3.7), and the final states are the complete set χ_i and χ'_i . It is straightforward though tedious to show that the splitting of levels creates fine structures in the f -electron spectral density near the Fermi energy, as also shown in Fig. 1. The peak at the Fermi energy remains singular. The satellites in both sides, which come from the matrix elements between bonding and antibonding levels, have rounded peaks due to the finite lifetime of the antibonding levels. Since $V \cong 0.2$ eV, it will require very high resolution to detect the fine structure by photoemission.

IV. ELECTRICAL RESISTIVITY AND SPECIFIC HEAT

The electrical resistivity of γ -Ce, β -Ce, and a number of Ce alloys and compounds exhibit Kondo-type temperature dependence. After subtracting out the phonon scattering contribution to the resistivity, the remainder decreases with increasing temperature over a range of temperature around 100 K. At low temperatures the electrical resistivity is well described by the Fermi-liquid model. The commonly accepted explanation of the Kondo behavior is the spin-flip scattering.^{1,10,11} The temperature at which the Fermi-liquid behavior turns into Kondo behavior is designated as the spin-fluctuation temperature T_{sf} . In this section we discuss the possibility that the Kondo behavior in the electrical resistivity may have a totally different origin. The f -electron spectral density shown in Fig. 1 has a singular peak at the Fermi level. The physical origin of this peak is the local d - f correlation. Mahan²⁶ was the first to point out that the problem of this so-called x-ray-edge singularity is mathematically equivalent to the Kondo problem. The isomorphism also implies that the x-ray-edge singularity in the f -electron spectral density can give rise to Kondo-type resistivity anomaly.

Owing to d - f hybridization the d electron acquires a self-energy correction

$$\Sigma_{\vec{k}}(\nu) = V^2 G_f(\nu), \quad (4.1)$$

where $G_f(\nu)$ is the f -electron propagator. The inverse lifetime of the d electron is related to the imaginary part of the self-energy, which in turn is proportional to the f -electron spectral density

$$\frac{1}{\tau(\nu)} = 2\pi V^2 \rho_f(\nu). \quad (4.2)$$

The electrical conductivity is proportional to the integral

$$\sigma(T) \propto \int \tau(\nu) \left[-\frac{\partial n(\nu)}{\partial \nu} \right] d\nu, \quad (4.3)$$

where $n(\nu) = (e^{\beta(\nu-\mu)} + 1)^{-1}$ is the Fermi distribution function and $\beta = (k_B T)^{-1}$. When the system is regarded as a collection of independent Ce sites, the f -electron spectral density has the singular behavior

$$\rho_f(\nu) = C_{\pm} | \nu - \mu |^{-\Delta}, \quad (4.4)$$

where the scale factors C_{\pm} refer to $\nu > \mu$ and $\nu < \mu$ re-

gions, respectively. Putting this result into Eqs. (4.2) and (4.3), we find that the leading temperature dependence of $\sigma(T)$ is $\sigma(T) \propto T^{\Delta}$, or the resistivity

$$\rho(T) \propto T^{-\Delta}. \quad (4.5)$$

This power law describes adequately the resistivity anomaly. This resistivity component has a lower power of V dependence than the spin-flip scattering contribution, so it is expected to be more important than the latter.

At low temperatures the resistivity saturates at the well-known unitarity limit. However, in ordered systems the f sites tend to become coherent at low temperatures and the resistivity anomaly is better described by the Fermi-liquid model.

The part of the f -electron spectral density near the Fermi level contributes to a temperature-dependent specific heat. In the independent f -site model the specific heat has the expression

$$C(T) = \int \rho(\nu) \nu [dn(\nu)/dT] d\nu. \quad (4.6)$$

At low temperatures

$$C(T) \propto T^{1-\Delta},$$

and at high temperatures

$$C(T) \propto T^{-2}.$$

Between the low-temperature limit and the high-temperature limit the specific heat has a maximum.

The position of the specific-heat maximum falls near a characteristic temperature T_c which can be estimated from the spectrum as follows. The integrated intensity under the singularity at ν_1 is

$$I_1 = (W - \omega_1)\mu / W(\mu - \omega_1) \quad (4.7)$$

for a band with a uniform density of states between 0 and W .¹⁹ We define T_c such that the integrated intensity between $\nu_1 - kT_c$ and ν_1 is one-half of I_1 . Taking the asymptotic expression for the spectrum in Eq. (4.4), we find

$$kT_c \cong W(I_1/2)^{1/(1-\Delta)}. \quad (4.8)$$

Based on the energy parameters deduced for Ce, we estimate $kT_c \cong 0.016$ eV or $T_c \cong 200$ K. The spin-fluctuation temperature for Ce systems range from 20 to 200 K. We speculate that for those systems with high T_{sf} the Kondo-type behavior may have its origin in d - f correlation rather than spin fluctuation.

Note added in proof. It has been pointed out to the authors that the calculation in Sec. III for mixed f^0 and f^1 states can be carried out more elegantly by the projection operator approach. See L. Mower, Phys. Rev. **142**, 799 (1966).

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APPENDIX: TWO-SITE INTERACTION

We create two f^0 sites at \vec{R}_1 and \vec{R}_2 in a lattice of f^1 sites. The Hamiltonian of the system is

$$H'_0 = \sum_{\vec{k}} \epsilon_{\vec{k}} d_{\vec{k}}^\dagger d_{\vec{k}} - \left[\frac{U}{N} \right] \sum_{\vec{k}, \vec{k}'} d_{\vec{k}}^\dagger d_{\vec{k}'} (e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_1} + e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_2}). \quad (\text{A1})$$

From previous discussion we expect that H'_0 can be diagonalized by a canonical transformation

$$c_n = \sum_{\vec{k}} a_{n\vec{k}} d_{\vec{k}}. \quad (\text{A2})$$

such that

$$[c_n, H'_0] = \omega_n c_n. \quad (\text{A3})$$

Putting Eqs. (A1) and (A2) into Eq. (A3), we find

$$(\epsilon_{\vec{k}} - \omega_n) a_{n\vec{k}} = \left[\frac{U}{N} \right] \sum_{\vec{k}'} (e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_1} + e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_2}) a_{n\vec{k}'}. \quad (\text{A4})$$

We define

$$A_n = \sum_{\vec{k}} a_{n\vec{k}} e^{-i\vec{k} \cdot \vec{R}_1}, \quad (\text{A5})$$

$$B_n = \sum_{\vec{k}} a_{n\vec{k}} e^{-i\vec{k} \cdot \vec{R}_2}. \quad (\text{A6})$$

We can then solve Eq. (A4) to obtain

$$a_{n\vec{k}} = \left[\frac{U}{N} \right] \frac{1}{\epsilon_{\vec{k}} - \omega_n} (A_n e^{i\vec{k} \cdot \vec{R}_1} + B_n e^{i\vec{k} \cdot \vec{R}_2}). \quad (\text{A7})$$

We substitute this result into the definitions of A_n and B_n to find two linear homogeneous equations for these two quantities. The condition that nonzero solutions exist is found to be

$$1 = \left[\frac{U}{N} \right] \sum_{\vec{k}} \frac{1 \pm \cos(\vec{k} \cdot \vec{R})}{\epsilon_{\vec{k}} - \omega_n}, \quad (\text{A8})$$

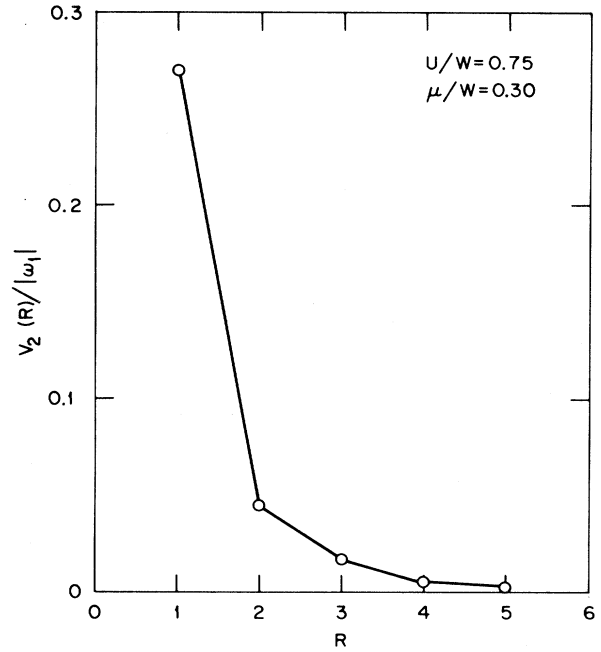


FIG. 2. Repulsive potential between two f^0 sites. Straight lines are drawn between points for different lattice distances to guide the eye.

where $\vec{R} = \vec{R}_1 - \vec{R}_2$. When the two sites are far apart, the cosine term in the above equation undergoes many oscillations as \vec{k} varies so that it makes negligible contribution to the integrals. In this case the problem reduces to that of two noninteracting sites.

We are particularly interested in the split-off states $\omega_1^{(\pm)}$, which are the solutions of Eq. (A8) below the continuum, because they contribute to the main part of the correlation energy. Thus we study the interaction between the two sites using the quantity

$$V_2(R) = \omega_1^{(+)} + \omega_1^{(-)} - 2\omega_1, \quad (\text{A9})$$

where ω_1 is defined in Eq. (2.8). To make the calculation of $\omega_1^{(\pm)}$ tractable we assume a one-dimensional linear dispersion relation $\epsilon_k = v|k|$ with $-\pi \leq k \leq \pi$. The distance between nearest neighbors is taken as unity. The result of the numerical analysis is shown in Fig. 2, in which $V_2(R)/|\omega_1|$ is plotted as a function of R . Since two f^0 sites cannot coincide, $V(0)$ is undefined. For nonzero R the quantity $V_2(R)$ is found to be positive, indicating repulsive interaction. The interaction strength decreases very rapidly such that when the two sites are three lattice distances apart, one makes a less than 2% error by treating them as noninteracting.

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