PHYSICAL REVIEW B VOLUME 26, NUMBER 4 15 AUGUST 1982

Theory of a mixed-valent impurity

T. V. Ramakrishnan*
Bell Laboratories, Murray Hill, New Jersey 07974

K. Sur
Department of Physics, Indian Institute of Technology, Kanpur 208016, India

(Received 5 November 1981)

We present a perturbative theory for the thermodynamic properties of a mixed-valent impurity in a metal. The impurity has two ionic configurations f^{n-1} and f^n (nondegenerate and n_λ-fold degenerate, respectively) with energies ϵ_0 and $(\tilde{\epsilon}_f+\mu)$, the difference $(\tilde{\epsilon}_f-\epsilon_0)$ being small. They mix via hybridization with conduction electrons (matrix element V_{kf}). We show that for $D>(\tilde{\epsilon}_f-\epsilon_0)\gtrsim -n_\lambda\Delta\ln(D/n_\lambda\Delta)$ a Brillouin-Wigner perturbation theory is convergent. Here $\Delta=|V_{kf}|^2\rho(\mu)$ is the virtual level width and $2D$ is the conduction-electron bandwidth, $\rho(\mu)$ being the density of states at the Fermi level. The expansion parameter is the inverse of the orbital degeneracy n_λ. Since this is large (6 to 8), the expansion is quite convergent, and the lowest-order theory is accurate. This is checked by calculation of higher-order terms for various values of $(\tilde{\epsilon}_f-\epsilon_0)$. In the above range of $(\tilde{\epsilon}_f-\epsilon_0)$ the f-electron number is seen to change from $(n-1)$ to about $(n-1)+0.80$, so that there is a perturbative theory for a strongly-mixed-valent impurity. Hybridization stabilizes the singlet f^{n-1} relative to f^n, the maximum stabilization energy (level shift) being approximately $n_\lambda\Delta\ln(D/n_\lambda\Delta)$ for $\epsilon_0=\tilde{\epsilon}_f$. This singlet ground state has been obtained variationally by Varma and Yafet, and from renormalization-group arguments by Haldane, and by Krishnamurthy, Wilkins, and Wilson; the Brillouin-Wigner perturbation theory has been used earlier by Bringer and Lustfeld. However, the recognition of $(1/n_\lambda)$ as an expansion parameter and the consequent simplification of the theory are new. Physical properties such as valence, susceptibility, and specific heat are calculated as a function of (k_BT/Δ) for various values of $(\tilde{\epsilon}_f-\epsilon_0)$. A simple way of including the effect of alloying pressure is described. Many characteristic properties of metallic dilute and concentrated mixed-valent systems, such as the temperature dependence of valence, the positive T^2 slope of the low-temperature susceptibility $\chi(T)$, the broad maximum in it, the relation between $\chi(0)$ and the Curie-Weiss temperature of high-temperature susceptibility, are qualitatively explained and quantitatively characterized for the first time. The results are directly applicable to dilute and nondilute alloys. They can also be applied to concentrated perfect lattice systems except at the lowest temperatures where relatively small intersite coupling leads to a uniform Fermi-liquid ground state. The Kondo limit, i.e., the nearly-f^n-valent singlet which occurs for $(\tilde{\epsilon}_f-\epsilon_o)\ll -n_\lambda\Delta$, is not described by the present theory.

I. INTRODUCTION AND SUMMARY

In the last decade or so, rare-earth-element ions of a large number of lanthanide metals, intermetallics, alloys, and compounds have been found to exist in a non-integral- (or mixed-) valent state. Normally, because of the smallness of the $4f$ orbital and its weak overlap with conduction-band states, the $4f$ ion retains its atomic identity; it is in its Hund's-rule, integral-valent ground state. However, in mixed-valent systems, two configurations, namely $4f^n$ (energy ϵ_f) and $4f^{n-1}$ (energy ϵ_0) plus a conduction electron at the Fermi level (energy μ) are energetically close. The difference $(\epsilon_f-\epsilon_0-\mu)$ is small, and the ion appears to fluctuate between two atomic configurations. Such systems exhibit a range of characteristic properties, such as absence of long-range magnetic order, a broad maximum in the magnetic susceptibility, heavy Fermi-liquid behavior at low temperatures, extreme sensitivity of electrical properties to disorder, etc., which are not well understood.[1-3] Theoretically the problem is difficult because of the need to describe simultaneously localized, strongly correlated f states, extended conduction-electron states, and transitions between them.

In this paper, we present a first-principles theory for the mixed-valent impurity,[4] i.e., for a single non-integral-valent ion in a metal. The impurity problem is of great importance in this field for several reasons. First, there is direct experimental evidence that many mixed-valent alloys behave like dense impurity systems. For example, the magnetic susceptibility of $Yb_{1-x}Y_xCuAl$ (Ref. 5) is proportional to the yttrium concentration x. The resistivity of $CePd_3$ is very sensitive to disorder, but the final resistivity of slightly disordered $CePd_3$ is the same in size and temperature dependence irrespective of the source of disorder, e.g., nonstoichiometry or metal-ion substitution.[6] This suggests that any kind of disorder breaks up electronic coherence, and if sufficient returns one to the dense impurity limit. Second, a number of dilute mixed-valent alloys, e.g., Eu in $ScAl_2$,[7] Ce in La_xTh_{1-x},[8] and Ce in Th,[9] have been experimentally studied. Their physical properties are found to be quite similar to those of concentrated systems[10] in many respects. Third, extension of methods used in our work to two impurities and to the lattice shows that in metallic strongly-mixed-valent systems, intersite coupling energies are smaller than single-site energies. Therefore their thermodynamics is accurately described by the independent impurity limit.[4] This idea has been used by one of us (Ramakrishnan) to discuss quantitatively[11] the mixed-valence phase transition in Ce and its alloys. To summarize, the independent impurity limit illuminates a number of properties of dense mixed-valent systems and is of direct experimental relevance.

We describe here a theory where the two ionic configurations are treated exactly and the admixture effect is treated perturbatively. The small admixture is characterized by a matrix element V_{kf} for transition from f^n to f^{n-1} plus a conduction electron in the state $\vec{k}$. The appropriate formalism (a many-body version of Brillouin-Wigner perturbation theory) was developed by Keiter and Kimball,[12] and was applied to the present problem by Bringer and Lustfeld[13] who obtained many of the results described here. It is not clear, however, that perturbation theory will work for mixed-valent systems, since even a small hybridization has a large effect when the configurations are close in energy, i.e., when V_{kf} is not much less than

$$|\epsilon_f-\epsilon_0-\mu| = |\tilde{\epsilon}_f-\epsilon_0| = |\tilde{\epsilon}_f| \;.$$

We show here that there *is* a small expansion parameter in the mixed-valence regime. It is $(1/n_\lambda)$ where n_λ is the orbital degeneracy of one of the configurations (f^n for concreteness; we assume f^{n-1} to be nondegenerate). This expansion parameter is essentially a phase space factor; intermediate states involving f^n are n_λ times as numerous as those involving f^{n-1}. If, in addition, they have similar energies (as happens when $|\tilde{\epsilon}_f| \approx 0$), the resulting corrections are in the ratio n_λ:1. Since for the lanthanides rare-earth n_λ varies from 6 to 8, this large-n limit is realistic.

The theoretical formalism is outlined in Sec. II. The partition function has rigorously the same form as in the absence of hybridization, but with the "bare" energy levels $\tilde{\epsilon}_f$ and ϵ_0 replaced by real renormalized energy levels $\tilde{E}_f$ and E_0. The Brillouin-Wigner series for these has a diagrammatic representation. $\tilde{E}_f$ and E_0 depend on temperature T and on model parameters, namely n_λ, $\tilde{\epsilon}_f$, virtual level width $\Delta\ [=|V_{kf}|^2\rho(\mu)]$, and conduction-electron bandwidth $2D$. In the lowest order (Sec. III) and for $T=0$, $E_0<\tilde{E}_f$ when $\tilde{\epsilon}_f \gtrsim -n_\lambda \Delta \ln(D/n_\lambda\Delta) = -\epsilon_c$, that is, the ground state is a singlet.[14,15] The stabilization energy has the maximum value of nearly ϵ_c for $\tilde{\epsilon}_f=0$ (where $\tilde{E}_f$ is n_λ times less), and decreases smoothly as $\tilde{\epsilon}_f$ decreases. The higher-order correction for E_0 (Sec. IV) is found to be of relative order $[n_\lambda \ln(D/n_\lambda)]^{-1} \approx \frac{1}{20}$ at $T=0$ and $\tilde{\epsilon}_f \gtrsim 0$. The correction increases smoothly as $\tilde{\epsilon}_f$ decreases, and for $\tilde{\epsilon}_f \simeq -\epsilon_c$, is about 25%. Calculation of valence (Sec. V A) shows that $\langle n_f \rangle$ changes in the regime $D>\tilde{\epsilon}_f \gtrsim -\epsilon_c$ from $(n-1)$ to $(n-1)+0.8$, and we therefore conclude that much of the mixed-valent regime is accurately described by lowest-order Brillouin-Wigner perturbation theory.

Renormalization-group[16] (RNG) and scaling[14,17] analyses of the asymmetric Anderson model ($n_\lambda=2$) suggest two regimes: For $\tilde{\epsilon}_f \gtrsim -\Delta \ln(D/\Delta)$ the magnetic configuration f^n is disfavored, the moment never forms, the relevant fixed point is qualitatively similar to f^{n-1}, and is described as empty orbital (f^0 for $n=1$)[16] or mixed valent.[14] For $\tilde{\epsilon}_f \lesssim -\Delta \ln(D/\Delta)$ the magnetic configuration is favored, the valence is high and nearly integral, and there is a weak residual exchange or Kondo coupling involving only the states of the f^n configuration. This leads to a Kondo singlet ground state. In the former regime, RNG analysis becomes difficult with nonuniversal behavior, marginal operators, etc., whereas in the latter regime it is very successful. The perturbation theory discussed here is simple and accurate for $\tilde{\epsilon}_f \gtrsim -\epsilon_c$ but does not, at least in low order, describe the

Kondo regime. However, it is in the former regime that there is a large range of valence (approximately 0 to 0.8) rather than in the latter (approximately 0.8 to 1.0). For $\epsilon_c \gtrsim \tilde{\epsilon}_f \gtrsim -\epsilon_c$, the most important effect is configurational admixture or fluctuation, whereas for $\tilde{\epsilon}_f \lesssim -\epsilon_c$, the configuration is essentially f^n, and spin fluctuations within this configuration are basic. The former is directly due to hybridization V_{kf}, whereas the Kondo-spin exchange is an effect of second order in V_{kf}. In both regimes, however, basic model parameters scale logarithmically with bandwidth D, so that a scaling theory is possible. In the mixed-valence regime the parameter is the effective f-level energy[14] and in the Kondo regime it is the effective exchange coupling J.

High orbital degeneracy is relevant in several ways. It increases the singlet stabilization energy n_λ-fold, and extends the mixed-valent regime by the same factor. Over this range, a perturbative (Brillouin-Wigner) theory is adequate, with $(1/n_\lambda)$ as the expansion parameter. We discuss later (Sec. V) the fact that in this local Fermi liquid, self-interaction effects are small, of relative order $(1/n_\lambda)$ in *both* mixed-valent and Kondo regimes. Anderson has stressed the significance of high orbital degeneracy and has recently discussed the ways in which $(1/n_\lambda)$ appears as an expansion parameter in the mixed-valence problem[18] for both the impurity and the lattice.

The single mixed-valent impurity is a good starting point for some properties of the lattice. However, the perfect-lattice ground state is not an incoherent superposition of impurity ground states. The qualitatively new effects of intersite coherence, such as a semiconducting ground state, resistivity of the pure metallic system vanishing as $T \rightarrow 0$, and development of a new, perhaps small energy or temperature scale for the Fermi liquid, are not discussed here.

We use here the lowest-order Brillouin-Wigner perturbation theory to calculate physical properties of the mixed-valent impurity as a function of $\tilde{\epsilon}_f$, n_λ, Δ, D, and temperature T (Sec. V). The valence n_v, specific heat $C_v(T)$, and susceptibility $\chi(T)$ are discussed, and calculated results are presented for typical values of $(\tilde{\epsilon}_f/\Delta)$ and (Δ/k_BT). (The results depend only weakly on D, and in practice n_λ does not vary much, being 6 for Ce and Sm, and 8 for Eu and Yb.) In comparisons with experiment, electrochemical or alloying pressure effects, describable as variations of $\tilde{\epsilon}_f$ with n_v, should be included. We show how this can be done simply. One should now be able to analyze experimental results in terms of meaningful microscopic parameters, check their consistency, and to make systematic predictions. Many general features of mixed-valent alloys, e.g., the ratio between $\chi(0)$ and the slope of $C_v(T)$ at low temperatures,[19,20] the ubiquitous positive T^2 slope in $\chi(T)$ near $T=0$, and the maximum in it are obtained and explained. In the concluding section (Sec. VI), we discuss some related questions, e.g., Fermi-liquid theory and phenomenological two-level models for the mixed-valent impurity.

II. PERTURBATION THEORY

A. The Hamiltonian

The two rare-earth-ion configurations can be represented as $|\lambda\rangle$ and $|0\rangle$. The former denotes the n_λ states of f^n, which are degenerate with energy ϵ_f. A magnetic field can lift the degeneracy, in which case the energy levels will be denoted as ϵ_λ. The latter, f^{n-1}, is nondegenerate, with energy ϵ_0 which can be set at zero without loss of generality since only $(\epsilon_f-\epsilon_0)$ is relevant. The Hamiltonian, written in terms of projection operators[21] in the basis $|\lambda\rangle, |0\rangle$, is

$$\begin{aligned}(H-\mu N)=&\sum_{\lambda}(\epsilon_f-\mu)X^i_{\lambda\lambda}+\epsilon_0 X^i_{00}\\&+\sum_{k,\sigma}(\epsilon_k-\mu)a^\dagger_{k\sigma}a_{k\sigma}\\&+\sum_{\lambda,k}(V_{k\lambda}e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}_i}X^i_{0\lambda}a^\dagger_{k\sigma}+\mathrm{H.c.})\ .\qquad(1)\end{aligned}$$

The first two terms describe the ion at site i; $X^i_{\lambda\lambda}$ projects it on to the state $|\lambda\rangle$ and X^i_{00} to the state $|0\rangle$. The third term describes conduction electrons in eigenstates $\vec{\mathrm{k}}$ with energy $\epsilon_{\vec{\mathrm{k}}}$. The last is a hybridization term whereby the ionic configuration changes by emission or absorption of a conduction electron. $V_{k\lambda}$ represents the matrix element schematically; a proper description with explicit regard for Hund's-rule correlation, symmetry conservation, etc., is given by Hirst[22] and by Müller-Hartmann.[23] The Hamiltonian (1) is obviously related to the Anderson Hamiltonian. The local orbital is n-fold instead of twofold degenerate and the on-site repulsion $U=\infty$, i.e., other configurations such as f^{n+1} and f^{n-2} are assumed to have such high energies compared to ϵ_f or ϵ_0 that they can be ignored. In lanthanides, experimentally $U \gtrsim 5$ eV so that the above configurations are quite far away in energy. The idea is to perform perturbation theory in configurational change, i.e., in $V_{k\lambda}$. This involves statistical averages over products of projection operators X_{ab} which are neither fermions nor bosons, since their (anti-) commutators are projection operators and not c numbers.[21] Consequently, there is no Wick's theorem, i.e., high-order products of such operators cannot be split up into products of uncorrelated pairs. The sequence of configurational changes is important. One thus does not have a Feynman diagrammatic theory, but a theory where processes are represented by time-ordered diagrams (Goldstone diagrams). The formalism has been developed by Keiter and Kimball,[12] and by Bringer and Lustfeld[13] based on the general theory due to Balian and de Dominicis.[24] We present here the results.

The grand partition function can be written in a quasiparticle form[24,25]

$$Z=e^{-\beta\Omega}=\mathrm{Tr}[e^{-\beta(H-\mu N)}]=Z_c\sum_i e^{-\beta E_i}\ , \tag{2}$$

where Z_c is the free-conduction-electron partition function, i denotes the states $|0\rangle$ and $|\lambda\rangle$, and the *real* statistical quasiparticle energies E_i are given by the Brillouin-Wigner equation

$$E_i=\epsilon_i+\Gamma_i(E_i)\ , \tag{3}$$

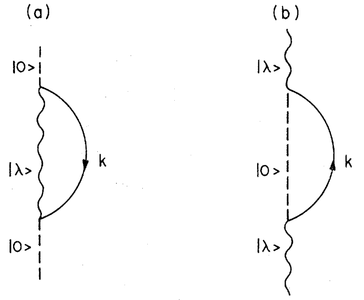

FIG. 2. Lowest-order Brillouin-Wigner terms for the energy shifts of the states (a) $|0\rangle$ and (b) $|\lambda\rangle$.

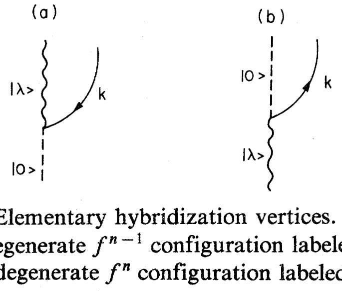

FIG. 1. Elementary hybridization vertices. In (a), an initial nondegenerate f^{n-1} configuration labeled $|0\rangle$ decays into a degenerate f^n configuration labeled $|\lambda\rangle$ and a conduction-band hole labeled k (dotted, wavy, and straight lines, respectively). (b) shows process $f^n \to f^{n-1}+$ conduction electron. Vertex has an amplitude $V_{k\lambda}$.

where $\Gamma_i(E_i)$ is the energy shift due to the perturbation, and can be calculated as follows: Draw diagrams with initial and final states i and *without only* i in the intermediate state. The state $|\lambda\rangle$ is denoted by a wavy line and $|0\rangle$ by a dotted line; the basic interaction vertex $V_{k\lambda}$ is shown in Fig. 1 where the conduction electron is absorbed [Fig. 1(a)] or emitted [Fig. 1(b)]. Starting from $|\lambda\rangle$ or $|0\rangle$, the only sequence of configurational changes allowed is flip-flops between them. Thus a general term consists of this sequence, and of band-electron lines joined in a particular way. The latter are represented by lines directed upwards [particles, energy ϵ_k, occupation factor $(1-f_k^-)$] or downwards (holes, energy $-\epsilon_k$, occupation factor f_k^-). An intermediate state m, corresponding to the interval between two successive interactions, has an energy E_m obtained by adding the f-configuration energy and electron energies. With this state, we associate an energy denominator (E_i-E_m). For example, we show in Fig. 2 the lowest-order Brillouin-Wigner corrections; these correspond to the equations

$$E_0=\epsilon_0+\sum_k \frac{f_k^-\,|V_{k\lambda}|^2}{E_0-(\epsilon_f-\epsilon_k)}\ , \tag{4a}$$

$$E_f=\epsilon_f+\sum_k \frac{f_k^+\,|V_{k\lambda}|^2}{E_f-(\epsilon_0+\epsilon_k)}\ . \tag{4b}$$

The next-order correction to E_0 is shown in Fig. 3

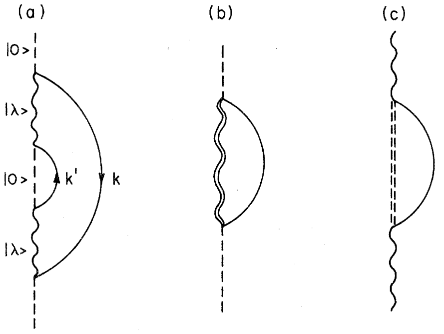

FIG. 3. Some higher-order energy-shift diagrams. (a) shows the only diagram corresponding to energy shift of the state $|0\rangle$ which is of fourth order in $V_{k\lambda}$. In (b), the double wavy line stands for the dressed intermediate-state ($|\lambda\rangle$) propagator which results on summing an infinite repeated sequence of diagrams for it, of which (a) is the first term. In (c) the double-dotted line is similarly the dressed $|0\rangle$-state propagator.

where the intermediate-state $|\lambda\rangle$ hybridizes with $|0\rangle$.

The lowest-order Brillouin-Wigner result [Eq. (4)] can be obtained in other ways. The variational ground-state approximation used by Varma and Yafet[15] for $n_\lambda=2$ is equivalent to Eq. (4a) at $T=0$. The diagrammatic method shows how the Brillouin-Wigner expression results from an infinite-order resummation of the Rayleigh-Schrödinger expansion in powers of $V_{k\lambda}$ and represents it in a compact, physical way. It is easy to look at higher-order terms (for an impurity as well as for the lattice) and to examine the possibility of a convergent theory. The many-body technique is the only one that can be extended to calculate response functions[4,26,27] and to the lattice.[4,27,28] In the Brillouin-Wigner theory, while nominally the expansion is in powers of $V_{k\lambda}$, the actual expansion parameter is not known *a priori,* since in Eq. (7a) for the energy shift E_0, it enters the right-hand side also as an intermediate-state energy, and thus is not given explicitly. [The Rayleigh-Schrödinger expansion gives a shift $-n_\lambda \Delta \ln(D/|\tilde{\epsilon}_f|)$ at $T=0$ for E_0 which diverges at $|\tilde{\epsilon}_f|=0$. Thus the expansion parameter is known, but diverges in the interesting regime.] We find the expansion parameter in Sec. IV by evaluating higher-order corrections to E_0 and $\tilde{E}_f$. We first discuss the lowest-order result Eq. (4) in the next section.

III. LOWEST-ORDER RESULTS

A. General form

The lowest-order expressions (4) are easily integrated, e.g., for a band of width $2D$ and density of states (per spin) $\rho(\mu)$. The result is

$$E_0=\epsilon_0+n_\lambda\phi(E_0-\tilde{\epsilon}_f)\ , \tag{5a}$$

$$\tilde{E}_f=\tilde{\epsilon}_f+\phi(\tilde{E}_f-\epsilon_0)\ , \tag{5b}$$

where energies are in units of $\Delta=|V_{k\lambda}|^2\rho(\mu)$ and

$$\phi(x)=-\ln\frac{D}{|x|}+\ln\frac{2\pi k_BT}{|x|}+\mathrm{Re}\psi\left[\frac{1}{2}+\frac{i|x|}{2\pi k_BT}\right]\ , \tag{6}$$

$\psi(y)$ being the digamma function. Equations (5a) and (5b) are to be solved for E_0 and $\tilde{E}_f$, and the free energy obtained using Eq. (2). Because Eq. (5) is basic, we give here a simple but accurate interpolation formula for $\phi(x)$, namely

$$\phi(x)\simeq-[\ln(2D/2\pi k_BT)-\tfrac{1}{2}\ln(1+4u^2)+(1+6u^2)^{-1}]\ , \tag{7}$$

where $u=(x/2\pi k_BT)$. The formula (7) is exact in the two limits $|u|\gg1$ and $|u|\ll1$ (low and high temperatures, respectively), and gives the leading low-temperature correction $(\frac{1}{24}u^{-2})$ exactly, and the high-temperature correction quite closely [the exact value is $-1.963+8.4u^2$, whereas the value from Eq. (7) is $-1.693+8u^2$]. It is accurate to within a few percent throughout.

B. Ground state

The zero-temperature limit of Eqs. (5) is simple:

$$E_0=\epsilon_0-n_\lambda\ln\frac{D}{|E_0-\tilde{\epsilon}_f|}\ , \tag{8a}$$

$$\tilde{E}_f=\tilde{\epsilon}_f-\ln\frac{D}{|\tilde{E}_f-\epsilon_0|}\ . \tag{8b}$$

For large energy differences between configurations $(|\tilde{\epsilon}_f|\gg1)$, the results Eq. (8) reduce to straight perturbation theory, i.e.,

$$E_0=\epsilon_0-n_\lambda\ln\frac{D}{|\tilde{\epsilon}_f|} \tag{9a}$$

and

$$\tilde{E}_f=\tilde{\epsilon}_f-\ln\frac{D}{|\tilde{\epsilon}_f|}\ . \tag{9b}$$

The ground state is a singlet for $\tilde{\epsilon}_f\gg1$ and is a magnetic multiplet for $-\tilde{\epsilon}_f\gg1$. For $\tilde{\epsilon}_f=\epsilon_0=0$, i.e., when the two configurations are degenerate, hybridization lowers the energy of the singlet n_λ times that of the multiplet. Further, to leading logarithmic order,

$$E_0=-n_\lambda\ln\left[\frac{D}{n_\lambda}\right]\ , \tag{10}$$

so that hybridization stabilizes the singlet by an energy much larger than Δ, the virtual level width. The factor n_λ is due to the number of degenerate f^n configurations with which f^{n-1} can admix, and the logarithm is due to the larger effect of lower-energy hole excitations. As mentioned in the Introduction, $n_\lambda\ln(D/n_\lambda)\sim20$ typically. As $\tilde{\epsilon}_f$ decreases from zero, E_0 and $\tilde{E}_f$ approach each other, and at approximately

$$\tilde{\epsilon}_f=-n_\lambda\ln(D/n_\lambda)=-\epsilon_c\ ,$$

they are equal. For $\tilde{\epsilon}_f<-\epsilon_c$, the ground state is a magnetic multiplet and has energy $\tilde{E}_f$. The singlet-multiplet crossover, which occurs at $\tilde{\epsilon}_f=0$ in the absence of hybridization, is pushed down to $-\epsilon_c$ in this order. Fig. 4 shows the ground-state energy as a function of $\tilde{\epsilon}_f$. The dotted line is the result in the absence of hybridization; the ground state is f^{n-1} with energy 0 for $\tilde{\epsilon}_f>0$ and is f^n with energy $\tilde{\epsilon}_f$ for $\tilde{\epsilon}_f<0$. The full line is the lowest-order Brillouin-Wigner result, the crossover point ϵ_c being shown by a dot.

C. High temperature

As temperature increases, thermal smearing reduces the effect of states close to the Fermi level. At sufficiently high temperatures, the low-energy cutoff is k_BT rather than the renormalized level shift. The quasiparticle energies are

$$E_0=-n_\lambda\left[\ln\left[\frac{D}{2\pi k_BT}\right]-1.96+8.4\left[\frac{E_0-\tilde{\epsilon}_f}{2\pi k_BT}\right]^2\right] \tag{11a}$$

for

$$|E_0-\tilde{\epsilon}_f|\ll 2\pi k_BT\ , \tag{11b}$$

and

$$\tilde{E}_f=\tilde{\epsilon}_f-\left[\ln\left[\frac{D}{2\pi k_BT}\right]-1.96+8.4\left[\frac{\tilde{E}_f}{2\pi k_BT}\right]^2\right] \tag{11c}$$

for

$$|\tilde{E}_f|\ll 2\pi k_BT\ . \tag{11d}$$

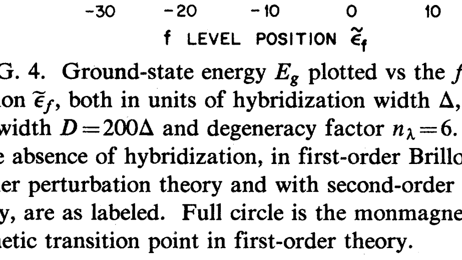

FIG. 4. Ground-state energy E_g plotted vs the f-level position $\tilde{\epsilon}_f$, both in units of hybridization width Δ, for bandwidth $D=200\Delta$ and degeneracy factor $n_\lambda=6$. E_g in the absence of hybridization, in first-order Brillouin-Wigner perturbation theory and with second-order theory, are as labeled. Full circle is the monmagnetic-magnetic transition point in first-order theory.

The level shifts are weakly temperature dependent. The high-temperature form [Eqs. (11b) and (11d)] is attained at $T_0\gtrsim|\tilde{\epsilon}_f|/2\pi k_B$ if the two configurations are far apart in energy, i.e., when $|\tilde{\epsilon}_f|\gg\epsilon_c$. Thermal degeneracy, namely population in the ratio $1{:}n_\lambda$, requires much higher temperatures

$$k_BT_B\gtrsim|E_0(T_B)-\tilde{E}_f(T_B)|\ ,$$

namely $k_BT_B\gtrsim|\tilde{\epsilon}_f|$. In the interesting mixed-valence regime $|\tilde{\epsilon}_f|<\epsilon_c$, T_0 varies only slowly with $\tilde{\epsilon}_f$, and the more stringent of the constraints (11b) and (11d) leads to $k_BT_0<3$ in the entire range $-15<\tilde{\epsilon}_f<10$ for $D=200$, $n_\lambda=6$. k_BT_0 is thus a factor of 5 to 10 less than the ground-state energy lowering $|E_0(T=0)-\tilde{\epsilon}_f|$ due to hybridization. The thermal degeneracy temperature T_B is somewhat higher but is still significantly less than $|E_0(T=0)-\tilde{\epsilon}_f|$. For example, at $\tilde{\epsilon}_f=0$, $k_BT_0=2.54$, $k_BT_B=10.0$, while $|E_0(0)|=15.6$, and at $\tilde{\epsilon}_f=-10$, $k_BT_0=1.4$, $k_BT_B=5.5$ with $|E_0(0)-\tilde{\epsilon}_f|=8.8$. Thus in the mixed-valence regime, even the thermal degeneracy temperature (times k_B) is substantially lower than the ground-state energy. This has the obvious consequence that the temperature scale over which the susceptibility, for example, changes, is smaller than that corresponding to the ground-state energy (see also Sec. V).

As temperature decreases, one smoothly passes over to the zero-temperature limit Eq. (8). The renormalized levels E_0 and $\tilde{E}_f$ are temperature dependent and can cross. For example, for $-\epsilon_c<\tilde{\epsilon}_f<0$, at high temperatures $\tilde{E}_f$ while at low temperatures E_0 lies below $\tilde{E}_f$. The effect of hybridization builds up as temperature is lowered, and pushes E_0 down.

D. Kondo effect

The lowest-order approximation leads to a magnetic ground state for $\tilde{\epsilon}_f<-\epsilon_c$. This is qualitatively incorrect since the ground state is a singlet.[14,16,29] In this Kondo regime, at very high temperatures $k_BT>|\tilde{\epsilon}_f|$, the configurations are degenerate; at lower temperatures, a local moment forms since the renormalized f^n configuration lies lower. This is the temperature regime described well by the above approximation. At exponentially lower temperatures,

$$T_K\sim\sqrt{D\Delta}\exp(\tilde{\epsilon}_f/n_\lambda\Delta)\ ,$$

transitions within the f^n manifold and associated conduction-electron scattering lead smoothly to a singlet. This effect is absent in low-order Brillouin-Wigner perturbation theory; perhaps infinite-order resummation is needed.

IV. HIGHER-ORDER PERTURBATION THEORY

As mentioned earlier, one does not *a priori* know the expansion parameter in a Brillouin-Wigner perturbation theory, especially when the initial states are quasidegenerate. We therefore calculate E_0 and $\tilde{E}_f$ (at $T=0$ for concreteness) to next order. The fourth-order term for E_0 is shown in Fig. 3(a), and describes the effect of hybridization on the intermediate-state $|\lambda\rangle$. Such a process occuring repeatedly shifts the intermediate-state energy, so that E_0, correct to the first two nonvanishing orders, is given by[13]

$$E_0=\epsilon_0-n_\lambda\int_0^D \frac{dx}{-E_0+\{\tilde{\epsilon}_f-\ln[D/(-E_0+x)]\}+x} \tag{12a}$$

and

$$\tilde{E}_f=\tilde{\epsilon}_f-\int_0^D \frac{dx}{-\tilde{E}_f+x+\{\epsilon_0-n_\lambda\ln[D/(-\tilde{E}_f+\epsilon_\lambda+x)]\}}\ . \tag{12b}$$

The logarithmic term in the energy denominator describes the higher-order shift. Vertex corrections appear in sixth order.

We have numerically calculated E_0 and $\tilde{E}_f$ using Eq. (12) for various values of $\tilde{\epsilon}_f$ with $n_\lambda=6$ and $D=200$ (in units of Δ). The results are shown in Fig. 4. The ground-state energy for $\tilde{\epsilon}_f=0$ differs by 3% from the lowest-order estimate. An analytical estimate is obtained by expanding the energy denominator in Eq. (12a), and retaining only the first correction to Eq. (8a). The error is seen to be of relative order $(1/|E_0-\tilde{\epsilon}_f|)$ where E_0 is the lowest-order Brillouin-Wigner result. At $\epsilon_\lambda=0$, this is

$$\left[n_\lambda \ln\left[\frac{D}{n_\lambda}\right]\right]^{-1}\simeq 0.04\ .$$

As $\tilde{\epsilon}_f$ decreases, the correction increases. The lowest-order stabilization energy $|E_0-\tilde{\epsilon}_f|$ is in error by 30% at $\tilde{\epsilon}_f\simeq-\epsilon_c$ and by 100% at $\tilde{\epsilon}_f\simeq-4n_\lambda$. The correction is always of one sign; namely the higher-order E_0 is lower than the lowest-order result. This can be understood in variational terms. The ground-state wave function leading to Eq. (8a) for E_0 now has, in addition to the Varma-Yafet term,[15] a term with an electron-hole pair, i.e., a term of the type

$$\sum_{kk'} c_{kk'}a_k^\dagger a_{k'}|0\rangle\ .$$

This improves the ground-state energy. We also note that the multiplet-singlet crossover energy is pushed to lower values of $\tilde{\epsilon}_f$. This is an expected level-repulsion effect due to the pushing apart of the intermediate configurational states [Eq. (12)] by hybridization effects.

The results of this section show that higher-order approximations such as Eq. (12) used by Bringer and Lustfeld[13] are of limited utility for calculating properties of mixed-valent systems, since if the higher-order term is important, this theory is poorly convergent.

V. PHYSICAL PROPERTIES OF THE MIXED-VALENT IMPURITY: VALENCE, SPECIFIC HEAT, AND SUSCEPTIBILITY

We now discuss the physical properties of the mixed-valent impurity in the lowest-order approximation.

A. Valence

The occupation probability of either configuration is a measure of the valence. We define it as the probability that f^n is occupied, i.e., the valence is

$$n_v=\left\langle \sum_\lambda X_{\lambda\lambda}\right\rangle\ . \tag{13a}$$

Obviously $n_v=1$ if the configuration is pure f^n and $n_v=0$ if it is pure f^{n-1}. Now, quite generally,

$$\left\langle \sum_\lambda X_{\lambda\lambda}\right\rangle=\frac{\partial\Omega}{\partial\tilde{\epsilon}_f}=P_0\frac{dE_0}{d\tilde{\epsilon}_f}+n_\lambda P_\lambda\frac{d\tilde{E}_f}{d\tilde{\epsilon}_f}\ . \tag{14}$$

Here P_0 and P_λ are the renormalized level-occupation probabilities, i.e.,

$$P_0=[e^{-\beta E_0}/(e^{-\beta E_0}+n_\lambda e^{-\beta \widetilde{E}_f})] \tag{15a}$$

and

$$P_\lambda=[e^{-\beta \widetilde{E}_f}/(e^{-\beta E_0}+n_\lambda e^{-\beta \widetilde{E}_f})] \,. \tag{15b}$$

E_0 and $\widetilde{E}_f$ are given by Eqs. (5a) and (5b), so that the derivatives in Eq. (14) are

$$\left[\frac{dE_0}{d\widetilde{\epsilon}_f}\right]=1-[1-n_\lambda\phi'(x)]^{-1}\Bigg|_{x=(E_0-\widetilde{\epsilon}_f)} , \tag{16a}$$

$$\left[\frac{d\widetilde{E}_f}{d\widetilde{\epsilon}_f}\right]=[1-\phi'(x)]^{-1}\Bigg|_{x=\widetilde{E}_f-\epsilon_0} . \tag{16b}$$

The level-shift integral $\phi(x)$ is given by Eq. (6) and from Eq. (7) $\phi'(x)$ is approximately

$$\phi'(x)=-\frac{4u}{2\pi k_B T}[\,(1+4u^2)^{-1}+3(1+6u^2)^{-2}] \,, \tag{17}$$

where $u=(x/2\pi k_B T)$.

The valence [Eq. (14)] is calculated by solving for E_0 and $\widetilde{E}_f$ [Eq. (8)] using, for example, the explicit form Eq. (7) for $\phi(x)$, and then Eqs. (15)–(17).

At low temperatures such that $k_B T \ll (-E_0+\widetilde{\epsilon}_f)$, the impurity is in the renormalized singlet state $|\widetilde{0}\rangle$ and the occupation of $|\widetilde{\lambda}\rangle$ is exponentially small. One then has

$$n_v=n_\lambda/(n_\lambda+\widetilde{\epsilon}_f-E_0) \,. \tag{18}$$

This is a function of n_λ and $\widetilde{\epsilon}_f$ (in units of Δ), and depends weakly (logarithmically) on D/Δ. We plot it in Fig. 5 as a function of $\widetilde{\epsilon}_f$ for $n_\lambda=6$ and $D/\Delta=200$. The valence fraction with the higher-order correction, namely that derived from Eq. (12a), is shown for comparison. It is clear that for $\widetilde{\epsilon}_f \gtrsim -\epsilon_c \simeq -16$, lowest-order perturbation theory is quite accurate. In this regime, n_v changes from 0 ($\widetilde{\epsilon}_f \gg \epsilon_c$) to 0.3 ($\widetilde{\epsilon}_f=0$) to 0.80 ($\widetilde{\epsilon}_f \simeq -\epsilon_c$), i.e., from low to almost integral high valence. The effect of hybridization on valence is strong, though it can be treated accurately in perturbation theory. For the special case of configurational degeneracy, i.e., $\widetilde{\epsilon}_f=0$, we find

$$n_v \simeq \ln(D/n_\lambda)/[1+\ln(D/n_\lambda)] \tag{19}$$

only weakly dependent on (D/n_λ). It is interesting that a valence ratio of approximately 2:1 or 3:1 for nondegenerate to degenerate always characterizes most strongly-mixed-valence systems, e.g., α-Ce, metallic SmS, and $\mathrm{SmB_6}$. If the two ionic configurations are degenerate (on an energy scale $n_\lambda\Delta$), so that Eq. (19) holds, a change of (D/Δ) by a factor of 4 (say from 200 to 50) changes n_v from 0.28 to 0.38 (for $n_\lambda=6$).

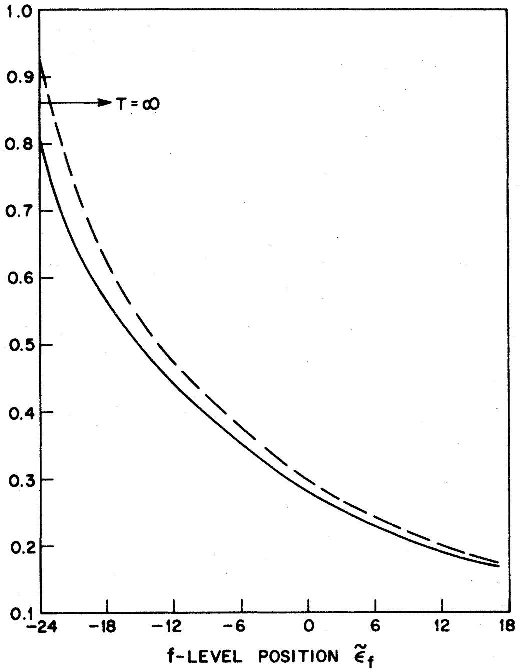

FIG. 5. Valence at zero temperature as a function of $\widetilde{\epsilon}_f$ (in units of Δ). Full curve is the first-order result and the dotted curve is the valence calculated from second-order perturbation theory.

We see (Fig. 6) that the decrease of valence with temperature is generally quite large; for example at $\widetilde{\epsilon}_f=0$, it decreases from 0.86 $(=\frac{6}{7})$ at high temperature ($T=\infty$) to 0.28 at zero temperature. Changes of this (and larger) size have been seen in Eu systems, e.g., dilute Eu in $\mathrm{ScAl_2}$,[7] as well as the intermetallics $\mathrm{EuCu_2Si_2}$ (Ref. 10) and $\mathrm{EuPd_2Si_2}$,[10] the valence being measured directly via the isomer shift or electric field gradient. In other systems, e.g., $\mathrm{Yb_{1-x}Y_xCuAl}$,[5] the valence is believed to change little from its $T=\infty$ value, and in some cases to even increase slightly with decreasing temperatures at low temperature.[30] This variety of behavior is due to an alloying pressure effect which we now discuss.

In the above calculation, we have assumed that $\widetilde{\epsilon}_f=(\epsilon_f-\mu)$ does not change when valence changes. This is unrealistic. As the valence decreases, the conduction-electron number increases correspondingly. In a metal this extra number stays in the vicinity of the impurity (approximately within a screening length). There is an increase in the electronic kinetic energy, as well as in the Coulomb attraction between the greater ionic charge and the conduction-electron charge. The total energy of the impurity system, i.e., its heat of solution or alloying, is a function of valence and therefore constrains the size of valence change. If the system is not infinitely dilute, the Fermi level goes up as valence decreases, so that $\tilde{\epsilon}_f$ decreases. This effect tends to reduce the valence change. For relatively small changes in the conduction-electron density, this alloying pressure effect is described by the equation

$$\tilde{\epsilon}_f(n_v)=\tilde{\epsilon}_f+\eta(1-n_v)\ , \tag{20}$$

$(1-n_v)$ being the extra conduction-electron number per impurity. For $\eta=0$, there is no alloying pressure and $\tilde{\epsilon}_f$ is constant. If the only effect is a Fermi-level shift,[20] $\eta=-c/\rho(\mu)<0$ where c is the concentration of mixed-valent ions and $\rho(\mu)$ the density of conduction-electron states at the Fermi level. However, other effects (e.g., increased Coulomb attraction) can make η less negative and change its sign. For $\eta>0$, there is a tendency to transfer charge to the host.

The valence of an impurity for two typical values of η is shown in Fig. 7. The f state is at the Fermi level, i.e., $\tilde{\epsilon}_f=0$ at high temperature. As temperature decreases, the valence decreases, and the f level is pushed down by alloying pressure for $\eta<0$. This tends to keep the valence constant, so that at $T=0$ (where $\tilde{\epsilon}_f\simeq-15$) the valence is 0.50 rather than 0.28. An interesting possibility is of an upturn in the valence at low temperatures. The valence change goes as T^2, the coefficient being proportional to

$$\left[1+\eta\frac{n_v^2(1-n_v)}{n_\lambda\Delta}\right]$$

so that for η sufficiently negative, the slope can be negative. For positive η, we see that as expected, the zero-temperature valence can be quite small, the f level having been pushed up ($\tilde{\epsilon}_f\simeq29$ at $T=0$) for $\eta=30$.

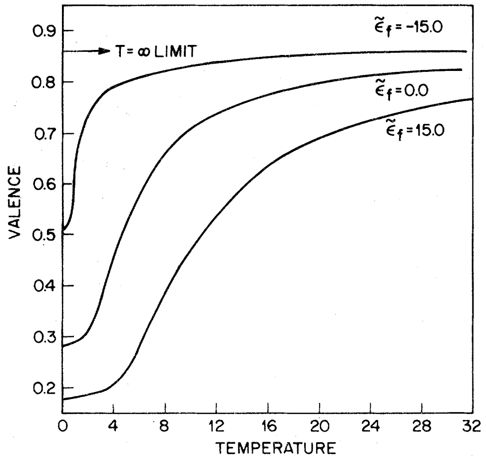

FIG. 6. Valence as a function of temperature (in units of Δ) for various values of $(\tilde{\epsilon}_f/\Delta)$ as shown. The high-temperature limit is indicated.

B. Specific heat

The specific heat C_v of a mixed-valent impurity is directly obtained from the Eqs. (2) and (3) for the thermodynamic potential. Using the standard thermodynamic formula $C_v=-T(\partial^2\Omega/\partial T^2)$, we see that it is expressed in terms of E_0, $\tilde{E}_f$, and its temperature derivatives. At low temperatures, only the renormalized singlet is occupied, and the specific heat is

$$C_v(T)=\frac{\pi^2}{3}n_v\frac{k_BT}{(-E_0+\tilde{\epsilon}_f)}\ . \tag{21}$$

The specific heat is linear in T as might be expected for a singlet ground state. A finite-temperature calculation shows a Schottky-type peak at about $T\simeq\frac{1}{2}\,|E_0-\tilde{\epsilon}_f|$.

C. Spin susceptibility

The ground state of the mixed-valent impurity is a singlet in which hybridization admixes the magnetic configuration f^n. It is therefore polarizable, i.e., its energy depends on the magnetic field. We calculate the polarizability as a function of temperature and explain the observed unusual but characterisitc $\chi(T)$, namely Curie-Weiss behavior at high temperatures, a maximum or broad hump at lower temperatures, and then a flattening out. In many systems, at still lower temperatures there is a rise in $\chi(T)$ and then saturation [e.g., $CeSn_3$ (Ref. 31) and $CeAl_3$ (Ref. 32)]. It is not clear whether this is an extrinsic effect due to impurities, or whether it is a lattice effect with a characteristically smaller energy scale.[18] The theory described here does not handle either possibility.

In a magnetic field, the energy levels of the degenerate configuration split, i.e.,

$$\epsilon_\lambda = \tilde{\epsilon}_f - g_J \lambda H \ ,$$

where g_J is the gyromagnetic ratio of the magnetic ion and λ the magnetic quantum number $[-J<\lambda \underset{\sim}{\leq} J$ and $(2J+1)=n_\lambda]$. Assuming no conduction-electron polarization, it is easy to show that the susceptibility is given by

$$\chi(T)=g_J^2 J(J+1)\frac{1}{3}\left[\frac{n_\lambda \phi''(x)}{1-n_\lambda \phi'(x)}\bigg|_{x=E_0-\epsilon_f} P_0 + \beta n_\lambda P_\lambda \right] , \qquad (22)$$

where $\phi(x)$ is the hybridization energy-shift function defined in Eq. (6). Using the approximate formula Eq. (7) for $\phi(x)$, the susceptibility $\chi(T)$ can be directly calculated once E_0 and $\tilde{E}_f$ are known. We now discuss the results for high and low temperatures.

1. High temperature

At temperatures so high that the levels are effectively degenerate $(T>\max[\epsilon_f, n_\lambda \ln(D/n_\lambda)])$, $P_0=1/(n_\lambda+1)$ and $P_\lambda=1/(n_\lambda+1)$, and

$$\chi(T)=\left[\frac{n_\lambda}{n_\lambda+1}\right]\tfrac{1}{3}g_J^2 J(J+1)\frac{1}{k_B T} \ , \qquad (23)$$

i.e., Curie law with a slightly $[n_\lambda/(n_\lambda+1)]$ reduced moment. Such a regime has been identified, for example, in Yb alloys[30] by noting that the valence ratio is close to $1{:}n_\lambda$. In good moment or Kondo systems, for $T \gg T_k$ (an exponentially small temperature), one has a Curie law without the factor $n_\lambda/(n_\lambda+1)$ since only the configuration f^n is occupied. At much higher temperatures, $T>|\tilde{\epsilon}_f|$, the above behavior occurs. The first correction as temperature is lowered has been calculated by Hewson[33] and by Lee and Chakravarty.[34] They find (for the case $n_\lambda=2$) that $\chi(T)=(A/T)[1-(\Theta/T)]$, where the Weiss

$$\Theta=\frac{\Delta\psi''(\tfrac{1}{2})}{\pi} \simeq 0.84\Delta \ . \qquad (24)$$

Our result for a general n_λ is that the Weiss Θ is the same, independent of n_λ. However, the Curie-Weiss form is valid only over a narrow temperature range.

The leading high-temperature correction[33,34] is a Kondo logarithm and not a Weiss (Θ/T^2) when $\tilde{\epsilon}_f \ll -n_\lambda \Delta$.

2. Low temperature

The ground state is a polarizable singlet, and the susceptibility is

$$\chi(T=0)=\chi(0)=\frac{1}{3}\frac{\mu_{\rm eff}^2 n_v}{|E_0-\tilde{\epsilon}_f|} \ , \qquad (25)$$

where $|E_0-\tilde{\epsilon}_f|$ is the singlet stabilization energy. The ratio of the susceptibility to specific heat has the noninteracting Fermi-gas value, i.e.,

$$\frac{\pi^2}{3}\frac{T\chi(0)}{C_v(\frac{1}{3})\mu_{\rm eff}^2}=W_0=1 \ . \qquad (26)$$

Including the next-order correction leads to the ratio[19]

$$W=1-\frac{\Delta}{|E_0-\tilde{\epsilon}_f|} \ . \qquad (27)$$

The deviation of this Wilson ratio from unity is a measure of the many-body effects in the local Fermi liquid. Clearly the effects are small for $\tilde{\epsilon}_f \gg -\epsilon_c$. In the Kondo limit, Nozieres and Blandin[35] find (for ions like Ce or Yb where one of the ionic configurations is nondegenerate) that

$$W=1+\frac{1}{n_\lambda-1} \ . \qquad (28)$$

To relative accuracy $(1/n_\lambda)$, one has a noninteracting local Fermi liquid for *all* $\tilde{\epsilon}_f$. This is probably why the phenomenological theory of Newns and Hewson[20] is successful.

For nonzero but low temperatures only the renormalized singlet is occupied (the contribution from $\tilde{E}_f$ is exponentially small) and one has

$$\chi(T)=\chi(0)\left[1+\frac{\pi^2\chi(0)^2(k_B T)^2}{(\mu_{\rm eff}n_v/3)^2}(2-n_v+\tfrac{1}{3}n_v^2)\right] . \qquad (29)$$

The most noteworthy thing is the positive slope of the T^2 term, a well-known feature of mixed-valent systems. The physical reason is the increase in singlet polarizability with temperature. The van Vleck polarizability depends inversely on the separation $|E_0-\tilde{\epsilon}_f|$ between the singlet ground state E_0 and the magnetic excited state $\tilde{\epsilon}_f$. This separation decreases as temperature increases, since the smoothening of the Fermi distribution reduces the effect of low-energy hole excitations and thus diminishes the hybridization lowering of E_0. We notice from Eq. (29) that the slope of the T^2 term is roughly proportional to $\chi(0)$ since n_v varies rather slowly with f-level position [e.g., as $\tilde{\epsilon}_f$ moves down from 0 to $-\epsilon_c$, $\chi(0)$ increases by a factor of 20 but n_v only by a factor of 2.5]. This dependence of the T^2 coefficient on $\chi(0)^2$ has been experimentally verified in studies of the $\mathrm{Ce(In}_x\mathrm{Al}_{1-x})_3$ system by Lawrence.[36] Lawrence and Beal-Monod[37] propose a paramagnon-theory explanation for this behavior. However, these systems are characterized by a low energy for valence or charge fluctuations. Since this occurs between magnetically different states, there is an attendant spin fluctuation. There is no indication of proximity to a ferromagnetic instability; the system is very strongly correlated, i.e., $(U/\pi\Delta)\simeq 10^2 \simeq \infty$, rather than close to unity (paramagnon regime). The paramagnon idea does not explain why the T^2 term is always positive. In that theory, the slope depends on derivatives of the f-band density of states, and could have either sign.

While there have been earlier numerical computations of the susceptibility in which a similar low-temperature curvature was found,[13,16] our work for the first time identifies the physical cause, provides an explicit expression for the term, and connects it with mixed valence.

We have briefly discussed, in the section on valence fraction (Sec. V A), the energetic constraint on valence change, parametrized by η. For a given η, the low-temperature susceptibility can be explicitly obtained, and is

$$\chi(T)=\chi(0)\left[1+\pi^2\left[\frac{k_BT}{E_0-\tilde{\epsilon}_f}\right]^2\left[2-n_v+\frac{n_v^3}{3}\right]\right]$$

$$-\chi(0)\frac{\pi^2}{3}\frac{(k_BT)^2 n_\lambda}{|E_0-\tilde{\epsilon}_f|^3}\left[\frac{n_\lambda}{|E_0-\tilde{\epsilon}_f|}+n_v(1-n_v)\right]\left[\frac{(1-n_v)^2(2-n_v)}{(n_v^2(1-n_v)+n_\lambda\eta^{-1})}\right]. \qquad (30)$$

The second term on the right-hand side is the correction which vanishes if $\eta=0$, i.e., if the change in valence does not affect $\tilde{\epsilon}_f$. If η is positive (i.e., valence tends to change), the positive slope is reduced while it is increased if η is negative.

In Fig. 8, we plot $\chi(T)$ vs T for some typical values of $\tilde{\epsilon}_f$, η being assumed zero. The maximum in $\chi(T)$ is quite prominent, and occurs at a lower temperature as $\tilde{\epsilon}_f$ decreases. The maximum is due essentially to thermal depopulation of the renormalized f level which reduces its Curie-type $(1/T)$ contribution exponentially with decreasing temperature. Using the form Eq. (22), the temperature of the maximum can be calculated to be

$$T_{\max}\simeq\tfrac{1}{2}\,|E_0-\tilde{\epsilon}_f|\ .$$

This fits the numerical results of Fig. 8 fairly well. The decrease at low temperatures is quite large, the ratio $[\chi_{\max}/\chi(T=0)]$ being typically 3 or 4. The mixed-valent system $\mathrm{YbAl_2}$ has a ratio of about 2.5.[20] In general, however, the ratio is in the range 1.3 to 1.4.[20] The reason most likely is the alloying pressure effect. We show for illustration in Fig. 9 the case $\eta=-20.0$, and $\tilde{\epsilon}_f=0.0$ at high temperatures. The susceptibility maximum (Fig. 9) shifts to a *much* lower temperature, and is not so prominent, the ratio $[\chi_{\max}/\chi(0)]$ being $\simeq 1.3$.

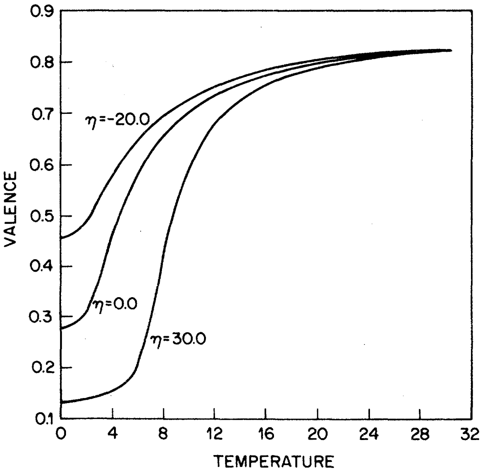

FIG. 7. Valence as a function of temperature (in units of Δ) for $\tilde{\epsilon}_f=0$, i.e., configurational degeneracy, for alloying pressures (in units of Δ) as shown.

VI. CONCLUDING REMARKS

We conclude by briefly discussing two alternative ways of describing the single mixed-valent im-

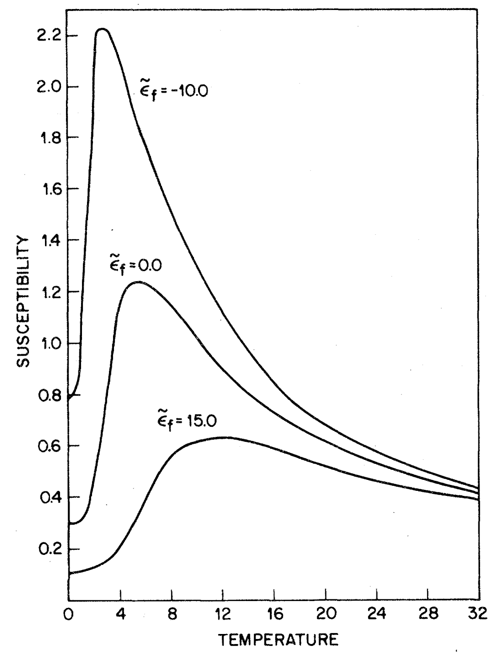

FIG. 8. Magnetic susceptibility, in units of $(\mu_{\rm eff}^2/\Delta)\times 10^{-2}$, as a function of temperature (k_BT/Δ) for three values of $(\tilde{\epsilon}_f/\Delta)$.

purity consisting of two atomic configurations which hybridize with the conduction band. One way is to integrate over the conduction-electron states so that one has a renormalized configuration picture. The other is exactly the opposite—the impurity is described entirely in terms of what it does to conduction-electron states, so that one has a local Fermi-liquid theory. Successful phenomenological models of both types exist, namely the configurational model of Sales and Wohlleben[38,39] and the local Fermi-liquid model of Newns and Hewson.[20] We summarize the general nature of these two types and comment on the phenomenological models.

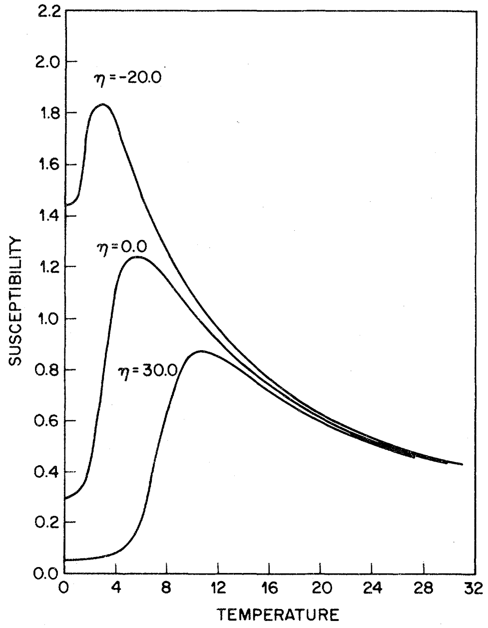

FIG. 9. Magnetic susceptibility, in units of $(\mu_{\rm eff}^2/\Delta)\times 10^{-2}$, as a function of temperature (k_BT/Δ) for $\tilde{\epsilon}_f = 0$ and three values of alloying pressure (in units of Δ).

A. Renormalized configuration theory

The partition function of the impurity has, rigorously, the same form as for nonhybridizing levels, i.e.,

$$Z = \left[e^{-\beta E_0} + \sum_{\lambda} e^{-\beta \tilde{E}_\lambda} \right],$$

where E_0 and $\tilde{E}_\lambda$ are renormalized configurational energies ("statistical quasiparticle" energies) shifted because of hybridization with respect to their bare atomic values ϵ_0 and $\tilde{\epsilon}_\lambda$. We have shown here that there is a simple convergent perturbation theory for E_0 and $\tilde{E}_\lambda$ in the mixed-valence regime. Physical properties such as valence and susceptibility can be written as a sum of terms, one for each configuration, and involve $E_0, \tilde{E}_\lambda$ and their derivatives. A quasiparticle state is obviously an admixture of bare configurational states. The renormalized levels are sharp. They are temperature dependent because the hybridization effect depends on temperature through conduction-electron occupation numbers. They can cross; for example, one can have $E_0 > \tilde{E}_\lambda$ at high temperatures and $E_0 < \tilde{E}_\lambda$ at low temperatures.

It is clear that not all physical properties can be described in terms of just the renormalized energies. For example, the f-electron excitation spectrum has a quasiparticle pole $\tilde{f}^{n-1} \to \tilde{f}^n$. It also has a continuum because the excitation $f^{n-1} \to f^n +$ (conduction-hole continuum) is possible within a quasiparticle state, say $\tilde{f}^{n-1}$. Excitation spectra and correlation functions can be calculated[4,26–28] for mixed-valent systems in perturbation theory, but they involve more details of hybridization.

The phenomenological models of Sales and Wohlleben[38] and Sales[39] emphasize, following Hirst[22] (and Schrieffer[40]), configurational persistence. The effect of valence admixture via hybridization with the conduction band is parametrized by an effective temperature $(T + T_s)$

or $(T^2+T_s^2)^{1/2}$ and Boltzmann statistics with this temperature.[38] T_s is a measure of the admixture effect. In later work, Sales[39] associates a width Γ_j with the level E_j (i.e., a Lorentzian density of states) and assumes that the configurations are thermally occupied according to Fermi statistics rather than Boltzmann statistics appropriate to such levels. In both models, the valence ratio is given by the relative thermal population of the broadened levels; they are not quasiparticle levels with some amplitude for both bare ionic configurations as discussed above. We do not find that the effect of hybridization can be described as done by Wohlleben and Sales. Nor can our final results for $\chi(T)$ or valence $n_v(T)$ be simply parametrized in terms of T_s or (E_j,Γ_j). The numerical parameters (E_j,Γ_j) deduced from fitting the susceptibility data, for instance, cannot be ascribed a basic significance, e.g., Γ_j as configuration fluctuation rate, or be compared with, say, spin lifetimes (i.e., width of $\chi(q,\omega)$).

B. Fermi-liquid theory

The hybridization between the f configuration and the conduction electrons affects the latter. At low temperatures, the state of the system is determined by hybridization effects to be a singlet so that there are no internal degrees of freedom to the impurity. Thus the state can be described entirely in terms of the effect on conduction electrons. If the local Fermi liquid has no self-interaction, then phase shifts $\delta_\lambda(\epsilon)$ in the f channel suffice.

It seems clear, as discussed in Sec. V C, that the self-interaction in the local Fermi liquid is weak, of relative order $(1/n_\lambda)$. The zero-temperature phase shifts satisfy the Friedel sum rule,

$$\frac{1}{\pi}\sum_{\lambda}\delta_\lambda(\epsilon_F)=\frac{n_\lambda}{\pi}\delta(\epsilon_F)=n_v\ , \tag{31}$$

where we have assumed that the phase shift in the n_λ channels are equal (as they are in the absence of a magnetic field). As emphasized by Newns and Hewson[20] $0<n_v<1$ and not the total number of f electrons. Newns and Hewson[20] describe the phase shift $\delta(\epsilon)$ by a resonant-level model with two parameters, a virtual level width $\Delta^{\rm RL}$, and an effective f-level position $\tilde{\epsilon}_f^{\rm RL}$. It can be shown that a correspondence $\Delta^{\rm RL}=\Delta$ and $\tilde{\epsilon}_f^{\rm RL}=(\tilde{E}_f-E_0)$ reproduces approximately the zero-temperature results of this paper. However, the resonant-level model is useful only for very low temperatures $k_BT \ll (\tilde{E}_f-E_0)$ since E_0 and $\tilde{E}_f$ depend on temperature both due to temperature-dependent effects of hybridization and alloying pressure. As the multiplet level $\tilde{E}_f$ is progressively occupied with increasing T, there is spin-disorder scattering of conduction electrons and the potential phase-shift parametrization becomes invalid. However, for ground-state and low-temperature properties it is a simple and physically attractive model.

We now outline the generalization of the results obtained here to the lattice. The intersite coupling as calculated in perturbation theory[3,26,28] appears to be small for strongly-mixed-valent systems and is only via the conduction electrons. By neglecting many-body correlations between singlet states at different sites, one has a band-structure problem where the conduction electron scatters from site to site, each site being a resonant level parametrized as above. This is the familiar transition-metal band-structure problem with the following special features. Because of the Friedel sum rule constraint [Eq. (31)], the f-excitation band is nearly empty, having at most one excitation per site. Secondly, the spin-orbit coupling energy $\lambda\vec{L}\cdot\vec{S}$ is much larger than Δ.[41] Direct evidence for this is the dependence of the susceptibility on the full atomic Hund's-rule moment rather than the spin-only moment. Thus the conduction-electron scattering is in channels with fixed m_J rather than fixed (m_1,m_s). This renormalized and modified band-structure problem is, we believe, a good first approximation to the strongly-mixed-valence lattice. It enables one to discuss such questions as the possibility of gaps in the density of states, origin of extreme sensitivity to disorder, effect of banding on energy, and the possibility of two temperature scales (Δ for the band Fermi energy and $n_\lambda\Delta$ for the single-impurity stabilization energy).

ACKNOWLEDGMENTS

The present form of this work results largely from the suggestion of P.W. Anderson that high orbital degeneracy is a key feature of the mixed-valence problem. One of us (T.V.R) is indebted to him for this as well as other insightful discussions of the problem, and for encouragement. Much of the work reported here was done while T.V.R. was a visitor at Princeton University, where his stay was supported in part by National Science Foundation Grant No. DMR 78-03015 and in part by the U.S. Office of Naval Research Grant No. N00014-77-C-0711. Discussions with B. Batlogg, A. Jayaraman, C. M. Varma, and the computational help of H. Greenside are thankfully acknowledged.

[*] Present address: Department of Physics, Indian Institute of Science, Bangalore 560012, India.

[1] For an early review, see C. M. Varma, Rev. Mod. Phys. 48, 219 (1976).

[2] *Valence Instabilities and Related Narrow-Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977).

[3] *Proceedings of the International Conference on Fluctuating Valence Solids, Santa Barbara, 1981,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981).

[4] This and related work has been described by one of us (T. V. Ramakrishnan) in *Proceedings of the International Conference on Fluctuating Valence Solids, Santa Barbara, 1981,* Ref. 3.

[5] W. C. M. Mattens, P. F. de Chatel, A. C. Moleman, and F. R. de Boer, Physica B 96, 138 (1979).

[6] P. Scoboria, J. E. Crow, and T. Mihalisin, J. Appl. Phys. 50, 1895 (1979).

[7] W. Franz, F. Steglich, W. Zell, D. Wohlleben, and F. Pobell, Phys. Rev. Lett. 45, 64 (1980).

[8] M. B. Maple and D. Wohlleben, in *Magnetism and Magnetic Materials—1973 (Boston),* Proceedings of the 19th Annual Conference on Magnetism and Magnetic Materials, edited by C. D. Graham and J. J. Rhyne (AIP, New York, 1974), p. 447.

[9] M. Luszik-Bhadra, M. J. Barth, H. J. Broksch, G. Netz, D. Riegel, and H. H. Bertschat, Phys. Rev. Lett. 47, 871 (1981).

[10] For results on Eu systems, see, for example, E. R. Bauminger, D. Freundlich, I. Nowik, and S. Ofer, Phys. Rev. Lett. 30, 1053 (1973) (EuCu$_2$Si$_2$); E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, J. Phys. C 14, L93 (1981) (EuPd$_2$Si$_2$).

[11] T. V. Ramakrishnan (unpublished).

[12] H. Keiter and J. C. Kimball, Int. J. Magn. 1, 233 (1971).

[13] A. Bringer and H. Lustfeld, Z. Phys. B 22, 213 (1977).

[14] F. D. M. Haldane, Phys. Rev. Lett. 40, 416 (1978).

[15] C. M. Varma and Y. Yafet, Phys. Rev. B 13, 2950 91976).

[16] H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, Phys. Rev. B 21, 1044 (1980).

[17] J. H. Jefferson, J. Phys. C 11, 3919 (1978).

[18] P. W. Anderson, in *Proceedings of the International Conference on Fluctuating Valence Solids, Santa Barbara, 1981,* Ref. 3.

[19] H. Lustfeld and A. Bringer, Solid State Commun. 28, 119 (1978).

[20] D. M. Newns and A. C. Hewson, J. Phys. F 10, 2429 (1980).

[21] J. Hubbard, Proc. R. Soc. London, Ser. A 277, 237 (1964).

[22] L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970).

[23] E. Müller-Hartmann, in *Electron Correlation and Magnetism in Narrow-Band Systems,* edited by T. Moriya (Springer, New York, 1981).

[24] See, for example, R. Balian and C. deDominicis, Ann. Phys. 62, 292 (1971).

[25] J. M. Luttinger and Y. T. Liu, Ann. Phys. 80, 1 (1973).

[26] N. Grewe and H. Keiter, Phys. Rev. 24, 4420 (1981).

[27] T. V. Ramakrishnan (unpublished).

[28] H. Keiter and N. Grewe, in *Proceedings of the International Conference on Fluctuating Valence Solids, Santa Barbara, 1981,* Ref. 3.
Ref. 3.

[29] The wave function corresponds to a nondegenerate state; however, the explicit form given by Varma and Yafet (Ref. 15) for it is not adequate in this regime, and needs to be generalized to include the f-level-shift effect, and spin-flip processes causing admixture between the degenerate f-orbital states.

[30] D. Wohlleben, in *Proceedings of the International Conference on Fluctuating Valence Solids, Santa Barbara, 1981,* Ref. 3.

[31] T. Tsuchida and W. E. Wallace, J. Chem. Phys. 43, 3811 (1965); S. K. Malik, R. Vijayaraghavan, S. K. Garg, and R. J. Ripmeester, Phys. Status Solidi B 68, 399 (1975).

[32] K. Andres, J. R. Graebner, and H. R. Ott, Phys. Rev. Lett. 35, 1779 (1975).

[33] A. C. Hewson, J. Phys. C 10, 4973 (1977).

[34] T-K. Lee and S. Chakravarty, Phys. Rev. B 22, 3609 (1980).

[35] P. Nozieres and A. Blandin, J. Phys. (Paris) 41, 193 (1980).

[36] J. M. Lawrence, Phys. Rev. B 20, 3770 (1979).

[37] M. T. Beal-Monod and J. M. Lawrence, Phys. Rev. B 21, 5400 (1980).

[38] B. C. Sales and D. K. Wohlleben, Phys. Rev. Lett. 35, 1240 (1975).

[39] B. C. Sales, J. Low Temp. Phys. 28, 107 (1977).

[40] J. R. Schrieffer, J. Appl. Phys. 38, 1143 (1967).

[41] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. 44, 1 (1981).