# Magnetic susceptibility of mixed-valence rare-earth compounds

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Many rare-earth compounds (e.g., Sm chalcogenides, YbAl<sub>3</sub>) exhibit temperature-independent magnetic susceptibility at low temperatures in their mixed valence phase despite the fact that the ionic configuration in at least one of the valences is such as to lead to a Curie-Weiss behavior. An essential feature of these compounds is that the Fermi level is pinned to the *f* levels. We first examine the effect of this feature in the Anderson model for an isolated impurity and find through a strong-coupling variational wave function as well as through a simple Green's-function treatment that the susceptibility is finite at  $T \rightarrow 0^{\circ}$ K and of order  $\mu^2/\Gamma$  where  $\Gamma$  is the virtual width of the *f* level corrected for correlation effects. For the compounds, a twoband ("f" and "d" with orbital degeneracies neglected) Hubbard-like model leads in the same treatment to a finite susceptibility at T = 0, where now  $\Gamma$  is essentially the *f*-*d* hybridization energy. Order-of-magnitude agreement with experiments is obtained with a reasonable value of the *f*-*d* mixing interaction. The physics of the finite susceptibility at T = 0 is the renormalization of the local moments by the conduction electrons which is strongest when the *f* levels are at the Fermi level.

### I. INTRODUCTION

Mixed-valence rare-earth compounds have been extensively investigated in recent years.<sup>1-4</sup> Indirect evidence from lattice-constant measurements<sup>5</sup> was the first to indicate a mixed-valence situation in Yb and Sm compounds. Further clear indication that two ionic valence states are present in such compounds is provided by the experiments of Campagna *et al.*<sup>6</sup> in which the x-ray photoelectron spectra of the two valence states are seen side by side, by photoemission<sup>7</sup> measurements and by isomer-shift measurements.<sup>1,8</sup>

The temperature dependence of the susceptibility<sup>3,4,9</sup> in these compounds has been somewhat of a puzzle, for although one of the two ionic configurations is magnetic, the susceptibility at low temperatures is essentially constant <sup>10</sup> while one would have naively expected a Curie-Weiss-type behavior. Following Hirst's work, <sup>11</sup> Maple and Wohlleben<sup>9</sup> conjectured that as the ion fluctuates between the two configurations, the hopping on and off of the electron in effect quenches the magnetic susceptibility. Although what physically seems to happen can be cast in these words, no proof that the susceptibility of a fluctuating-valence system is finite at zero temperature has been previously given.

We give here a simple model for mixed-valence compounds and calculate the magnetic susceptibility. The physical idea is that, since in the ground state the  $f^n$  and  $(f^{n-1} + \text{conduction electron})$  configurations are both present, their energies must be very close (i.e., the difference must be of the order of the hopping linewidth). The extra electron is assumed to go into an extended state, so its energy is equal to the Fermi energy. The extra available f orbital can then be described by a localized state, with energy  $\epsilon_f$  nearly equal to to the Fermi energy  $\zeta$ , and which can accept one electron but not two.

The organization of this paper is as follows: In Sec. II we first discuss the single-impurity problem with a variational method for the ground state and then discuss the finite-temperature effects using a Green's-function decoupling scheme. The manner of derivation emphasizes how a singlet state is formed as the impurity level is brought close to the Fermi level. In Sec. III we treat the case when the f levels form a band which is close to the Fermi level. The interesting point is that, in the strong-coupling situation imposed by this condition, the behavior of the f band is not qualitatively very different from that of isolated f impurities. We conclude with a discussion of our results.

#### **II. SINGLE-IMPURITY PROBLEM**

For a single rare-earth ion in a sea of conduction electrons the following Anderson Hamiltonian describes the model:

$$\begin{aligned} \mathfrak{B} &= \sum_{k,\sigma} \quad \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k,\sigma} V_{kf} (c_{k\sigma}^{\dagger} c_{f\sigma} + c_{f\sigma}^{\dagger} c_{k\sigma}) \\ &+ U n_f \cdot n_{f1} + \sum_{\sigma} \epsilon_{f\sigma} c_{f\sigma}^{\dagger} c_{f\sigma} = \mathfrak{B} c_k + \mathfrak{B} c_{kf} + \mathfrak{B} c_f , \end{aligned}$$
(1)

where  $\epsilon_k$  is measured with respect to  $\zeta$ , the dependence of  $\epsilon_{f\sigma}$  on  $\sigma$  takes into account the Zeeman energy in an external field,  $\Re_z = \sigma_\mu H$ ,  $\sigma = \pm 1$ , the orbital degeneracy of the *f* electron is neglected thus replacing it by an *s* electron, and spherical *s* waves are used for the conduction electrons. The Zeeman energy of the conduction electrons is neglected. The value of *U* is assumed arbitrarily large. Let  $\Gamma = \pi V_{kf}^2 \rho(\zeta)$  be the virtual-level half-

2950

width where  $\rho(\xi) = Rk_{\xi}/2\pi\zeta$ , R being the radius of the specimen which is assumed to be spherical, and  $k_{\xi}$  the Fermi wave number. We assume that near the Fermi level the mixing matrix element between the local level and a plane wave  $\vec{k}$  is  $V_{kf}^2 = v/\sqrt{N}$ , where N= number of unit cells. Then, for spherical waves,  $V_{kf} = vk(\Omega/2\pi R)^{1/2}$  where  $\Omega$ is the unit-cell volume.

We will first construct a singlet wave function which will make it plausible that the susceptibility approaches a constant value as  $T \rightarrow 0$ °K. (This wave function is the analog, for the Anderson model, of Yosida's<sup>12</sup> wave function for the s-d model.) Let  $|\Psi_0\rangle = \prod_{k=0}^{k_c} c_{k}^{\dagger} c_{k}^{\dagger} |0\rangle$  be the ground state of  $\mathcal{K}_k$ . The following form is assumed for the ground state of  $\mathcal{K}_i$ :

$$\left|\Psi\right\rangle = a_{0}\left|\Psi_{0}\right\rangle + \sum_{k} a_{k} \left(c_{f\dagger}^{\dagger} c_{k\dagger} + c_{f\downarrow}^{\dagger} c_{k\downarrow}\right) \left|\Psi_{0}\right\rangle, \quad (2)$$

i.e.,  $|\Psi\rangle$  is a linear combination of  $|\Psi_0\rangle$  and of states obtained by transferring a single conduction electron to the localized state.  $|\Psi\rangle$  allows for perfect correlation, i.e.,  $n_{f_i}, n_{f_i} |\Psi\rangle = 0$ ; thus it is expected to be a good approximation as  $U \rightarrow \infty$ . Define

$$E_{-} = \langle \Psi | \mathcal{H} | \Psi \rangle \equiv E_{0} + \epsilon_{f} + \epsilon , \qquad (3)$$

where  $E_0$  is the unperturbed energy of  $|\Psi_0\rangle$  and  $\epsilon$  is to be determined. The variational equations for the coefficients  $a_0$ ,  $a_k$  are

$$\epsilon a_0 = - \epsilon_f a_0 + \sum_k \sqrt{2} V_{kf} a_k , \qquad (4a)$$

$$\epsilon a_k = \sqrt{2} \, V_{kf} a_0 - \epsilon_k a_k. \tag{4b}$$

Using (4b), the  $a_k$  are eliminated from (4a) and one obtains the eigenvalue equation,

$$\epsilon = -\epsilon_f + \sum_k \frac{2V_{kf}^2}{\epsilon + \epsilon_k} \quad . \tag{5}$$

Since all the  $\epsilon_k$  are negative, a negative solution always exists for  $\epsilon$ , and, for a free-electron band, using the expression of  $V_{kf}$  given above, one obtains

$$\epsilon = -\epsilon_f - \frac{2}{\pi} \Gamma\left(\ln \frac{4\zeta}{|\epsilon|} - 2\right). \tag{6}$$

If the virtual level is at the Fermi level,  $\epsilon_f = 0$ , the binding energy becomes of the order of  $\Gamma$ , provided  $\Gamma$  is small compared to the bandwidth. This means that the Kondo energy is in fact of the order of  $\Gamma$ .

As a test on our variational solution we now look at what happens when  $\epsilon_f$  sinks below the Fermi level and  $\Gamma \ll |\epsilon_f|$ . Then, for (6),  $|\epsilon|$  must become very small for the second term to overcome the positive first term, and it approximately satisfies  $-\epsilon_f = (2/\pi)\Gamma \ln(4\zeta/|\epsilon|)$ . Solving for  $\epsilon$ ,  $\epsilon = -4\zeta \exp[1/J\rho(\zeta)]$  where  $J = (2v^2/\epsilon_f)(k_f^2 \Omega/2\pi R)$ is the covalent-mixing exchange integral as given by the Schrieffer-Wolff transformation for  $U \rightarrow \infty$ . Thus  $\epsilon$  correctly reproduces the Kondo energy as given by the s-d model for this case. (A Kondo energy of the order of  $\Gamma$  is not obtainable from the s-d model since the latter is not an approximation to the Anderson Hamiltonian when  $|\epsilon_f| < \Gamma$ .) To obtain the susceptibility, we include a magnetic field H. The coefficients of  $c_{f}^{\dagger}c_{k}$ , and  $c_{f}^{\dagger}c_{k}$ , in (2) can no longer be taken equal. Writing equations analogous to (4) in this case, one obtains for the ground-state energy to order  $H^2$ :  $\epsilon(H) = \epsilon + G \mu^2 H^2$ where  $G = [2\epsilon(1 + \pi |\epsilon|/2\Gamma)]^{-1}$ . When  $\epsilon_f \simeq 0$ , the susceptibility at 0 °K is of order  $\chi \sim \mu^2/\Gamma$ . This result was to be expected for a singlet ground state.

Our variational wave function does not include states obtained from (2) by promoting the f electron to a state above the Fermi level. One would think that such states would further contribute to the binding of the singlet state and this is in fact the case. However, these states also contribute binding energy to the triplet state that can be constructed with the localized level. These contributions to the binding energy would be equal for the singlet and triplet states if  $a_0$  in (2) were zero, since the triplet state has no component in  $|\psi 0\rangle$ . In fact,  $a_0 = [1 + \ln(E_F/|\epsilon|)]^{-1/2}$  when  $\epsilon_f = 0$  and becomes rapidly smaller if the energy of the localized level sinks below the Fermi level, so the relative singlet-triplet energy shift due to single electron-hole pair excitations is small compared to the energy shift (6).

To calculate the susceptibility at finite temperatures and also to treat the case of a periodic array of f levels, we have performed a Green's-function calculation for the Hamiltonian (1), using Hubbard's decoupling scheme.<sup>13</sup>

The equation for the Fourier transform of the retarded Green's function  $\langle \langle c_{f\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega}$  is (taking  $\hbar = 1$ )

$$\omega \langle \langle c_{f\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega} = 1 + \sum_{k} V_{kf} \langle \langle c_{k\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega}$$

$$+ \epsilon_{f\sigma} \langle \langle c_{f\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega} + U \langle \langle n_{f-\sigma} c_{f\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle.$$

$$(7)$$

The second term on the right is eliminated by the relation

$$\langle \langle c_{k\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega} = [V_{kf}/(\omega - \epsilon_k)] \langle \langle c_{f\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega}, \quad (8)$$

and the last term is calculated from its equation of motion, making use of Hubbard's approximation<sup>13</sup>:

$$\langle \langle n_{f-\sigma} c_{k\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega} \simeq \langle n_{f-\sigma} \rangle \langle \langle c_{k\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega} , \qquad (9)$$

where  $\langle n_{f-\sigma} \rangle$  is the thermodynamic average of  $n_{f-\sigma}$ .

The decoupling (9) is in fact a very crude approximation: Unlike the case of the variational wave function which gave correctly the Kondo energy (and the magnetic susceptibility) when the localized level energy was placed well below the Fermi level  $(-\epsilon_f \gg \Gamma)$ . The decoupling (9) fails to give the correct answer in this case and predicts a small value  $\sim \mu^2/|\epsilon_f|$  for the 0°K susceptibility. This is not really surprising because the calculation of the susceptibility when  $-\epsilon_f \gg \Gamma$  requires a very careful and systematic decoupling of the equations of motion as the Curie law (for  $T > T_k$ , the Kondo temperature), as pointed out by Hamann, <sup>14</sup> is due to the small d state tail at the Fermi surface. Since we are interested in the opposite case  $|\epsilon_t| \leq \Gamma$  where the occupation of d states at the Fermi level is not small, it is plausible that the method of decoupling is not so critical here.

Substituting (9) and (8) into (7) and taking the limit  $U \rightarrow \infty$  we obtain

$$\langle \langle c_{f\sigma}; c_{f\sigma}^{\dagger} \rangle \rangle_{\omega} = \frac{1 - \langle n_{f-\sigma} \rangle}{\omega - \epsilon_{f\sigma} + i \Gamma(1 - \langle n_{f-\sigma} \rangle)} .$$
(10)

The factors  $\langle n_{f-\sigma} \rangle$  in this expression arise from the Coulomb repulsion. From (10) the occupation probability of the *f* orbital and the magnetic susceptibility are obtained by standard methods.<sup>13</sup> In terms of the narrowed halfwidth  $\overline{\Gamma}_{\sigma} = \Gamma(1$  $- \langle n_{f-\sigma} \rangle)$  we find at 0 °K

$$\langle n_{f\sigma} \rangle = (1 - \langle n_{f-\sigma} \rangle) \left( \frac{1}{\pi} \arctan \frac{\zeta - \epsilon_{f\sigma}}{\overline{\Gamma}_{\sigma}} + \frac{1}{2} \right) .$$
 (11)

In the absence of a magnetic field  $\epsilon_{f\sigma} = \epsilon_{f-\sigma}$  and  $\langle n_{f\sigma} \rangle = \langle n_{f-\sigma} \rangle \equiv n_f$ ; the two equations (11) reduce to a single one,

$$n_f = (1 - n_f) C,$$
 (12)



FIG. 1. Temperature dependence of the susceptibility of the localized state for  $\epsilon_f = \xi$ . The abscissa is  $\frac{3}{2}(kT/\Gamma)$ , the ordinate  $\chi_{\rm at} \Gamma/3\mu^2$  where  $\mu$  is the magnetic moment.



FIG. 2. Temperature dependence of the atomic susceptibility and of the occupation number  $2n_f$  of the localized state for  $\xi - \epsilon_f = 0.62\Gamma$ .

where 0 < C < 1. The maximum occupation of the localized level is thus  $2n_{f,\max} = 1$ , reflecting the maximum correlation brought about by an infinite U.

At finite temperatures  $\beta = 1/kT$ , the occupation number  $n_f$  is given by

$$\frac{n_f}{1-n_f} \equiv A_f = \int f(\omega) \, \frac{1}{\pi} \, \frac{\overline{\Gamma}}{(\omega-\epsilon_f)^2 + \overline{\Gamma}^2} \, d\omega, \qquad (13)$$

where  $f(\omega) = (e^{\beta\omega} + 1)^{-1}$ . As long as  $|\zeta - \epsilon_f| \leq \Gamma$ , the value of  $n_f$  at high  $T \leq \Gamma/k$  approaches the value  $\frac{1}{2}(2S+1)/2(S+1) = \frac{1}{3}$ .

The magnetic susceptibility is obtained by differentiating with respect to *H* the expression of  $\langle n_{f\sigma} \rangle$  at finite temperature. Letting  $\langle n_{f\sigma} \rangle = n_f - \sigma \alpha (\mu H) / \overline{\Gamma}$ , the atomic susceptibility is

$$\chi_{\rm at} = 2\alpha\mu^2/\overline{\Gamma}$$
,

and we find

$$\frac{\alpha}{\Gamma} = \left(1 - \frac{\overline{\Gamma}}{1 - A_f} \frac{dA_f}{d\overline{\Gamma}}\right)^{-1} \frac{1}{1 - A_f^2} \\ \times \int \left(-\frac{\partial f}{\partial \omega}\right) \frac{1}{\pi} \frac{\overline{\Gamma}}{(\omega - \epsilon_f)^2 + \overline{\Gamma}^2} d\omega .$$
(14)

In this expression the first term on the right-hand side is due to the dependence of  $\overline{\Gamma}_{\sigma}$  on *H* and the second term is due to the factor  $(1 - \langle n_{f-\sigma} \rangle)$  which appears in (11) and in the corresponding expression at finite temperature.

The first term reduces to 1 at all temperatures if  $\epsilon_f = \zeta$ . At high *T*, provided  $|\zeta - \epsilon_f| < \Gamma$ , the value of  $A_f$  approaches  $\frac{1}{2}$  and the first term approaches unity again. At 0 °K,  $dA_f/d\overline{\Gamma} \leq 0$  depending on whether  $\epsilon_f \leq \zeta$ , so for  $kT < \overline{\Gamma}$  the first factor increases with *T* if  $\epsilon_f < \zeta$  and decreases with *T* if  $\epsilon_f > \zeta$ . The second factor varies with *T* in the same way through the dependence of  $A_f$  on *T*. As a result, the temperature behavior of  $\chi_{at}$  depends on the parameter

 $b = (\xi - \epsilon_f)/\Gamma$ . If  $b \le 0$  the susceptibility decreases monotonically with temperature as shown on Fig. 1 for the value b = 0. If on the other hand b is positive and not too small,  $\chi_{at}$  first rises as Tincreases, reaches a maximum, and at higher Tbecomes Curie-Weiss like. Near T=0 it always varies quadratically in T. Figure 2 shows the occupation number  $2n_f$  and the susceptibility as functions of temperature for b = 0.62.

It is seen that  $2n_f$ , which corresponds to the fraction of trivalent character of the rare-earth ion, varies in this case from 0.86 to 0.7 while  $\chi_{at}$  has a maximum at  $kT \approx \frac{1}{5}\Gamma$ . It is amusing to note that this curve has features similar to the experimental curve of Havinga *et al.*<sup>4</sup> for YbAl<sub>3</sub>. However, a quantitative comparison is not warranted on two counts: (a) The Yb<sup>3+</sup> ion has  $J = \frac{7}{2}$  instead of  $\frac{1}{2}$  and the levels are split by the crystal field.<sup>15</sup> These effects can be included in the present calculation but this will not be done here. (b) The single-ion treatment is not applicable because the ions form a lattice. This case is now treated by the same method as above.

# III. PERIODIC ARRAY OF f LEVELS

The Hamiltonian of a lattice of rare-earth ions is

$$\Im C = \sum_{i,j,\sigma} T_{ij} c^{\dagger}_{si\sigma} c_{sj\sigma} + \sum_{ij\sigma} t_{ij} (c^{\dagger}_{si\sigma} c_{fj\sigma} + c^{\dagger}_{fj\sigma} c_{si\sigma}) + \sum_{i\sigma} \epsilon_{f\sigma} c^{\dagger}_{fi\sigma} c_{fi\sigma} + \sum_{i} U n_{fi}, n_{fi}, , \qquad (15)$$

where there is a broad "s" band characterized by



FIG. 3. 0°K susceptibility for the two-hand model as function of the position of the Fermi level. The localized level energy is at  $\epsilon_f = 0.4D$  above the bottom of the "s" band and  $s^2 \equiv 4t^2(1 - n_f)/D^2 = 0.016$ . The abscissa is the Fermi energy measured in units of the bandwidth D, the ordinate is  $\chi_{\rm at} D/\mu^2$ .



FIG. 4. Temperature dependence of the susceptibility for  $\epsilon_f = 0.5D$  and  $s^2 = 0.004$ . The abscissa is  $2kT/s^2D$ , the ordinate is  $\chi_{\rm at} D/2\mu^2$ . The Fermi energy  $\xi$  is in the middle of the gap.

the hopping integrals  $T_{ij}$  between sites *i* and *j*, the atomic *f* levels have energy  $\epsilon_{f\sigma}$  and correlation energy *U*, and there is a mixing term  $t_{ij}$  between *f* and "s" orbitals located on different sites  $i \neq j$ . Using the same decoupling approximation as above, the Green's function for the *f* band is found to be

$$G_{\sigma}^{ff}(\vec{q}, \omega) = (1 - \langle n_{-\sigma}^{f} \rangle) \frac{\omega - \epsilon_{s\vec{q}}}{(\omega - \epsilon_{f\sigma})(\omega - \epsilon_{s\vec{q}}) - t_{\vec{q}}^{2}(1 - \langle n_{-\sigma}^{f} \rangle)},$$
(16)

where

$$\begin{split} G_{\sigma}^{ff}\left(\vec{\mathbf{q}},\omega\right) &= \sum_{n} \left\langle \left\langle c_{fi\sigma} ; c_{f,i+n,\sigma}^{\dagger} \right\rangle \right\rangle_{\omega} e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{R}}_{n}}, \\ \epsilon_{s\vec{\mathbf{q}}} &= \sum_{n} T_{i,i+n} e^{i\vec{\mathbf{q}}\cdot\vec{\mathbf{R}}_{n}}; \\ t_{\vec{\mathbf{q}}} &= \sum t_{i,i+n} e^{i\mathbf{q}\cdot\vec{\mathbf{R}}_{n}}, \end{split}$$

and the factor  $1 - \langle n_{-\sigma}^f \rangle$  occurs in two places, just as in Eq. (10).

The spectral density function is

$$-\frac{1}{\pi} \operatorname{Im} G_{\sigma}^{ff}(\mathbf{\dot{q}}, \omega) = \frac{1 - \langle n_{\sigma}^{f} \rangle}{\tilde{\epsilon}_{u\mathbf{d}\sigma} - \tilde{\epsilon}_{l\mathbf{d}\sigma}}$$

$$\times \left[ \left( \tilde{\epsilon}_{u\bar{d}\sigma} - \epsilon_{s\bar{d}} \right) \delta(\omega - \tilde{\epsilon}_{u\bar{d}\sigma}) + \left( \epsilon_{s\bar{d}} - \tilde{\epsilon}_{l\bar{d}\sigma} \right) \delta(\omega - \tilde{\epsilon}_{l\bar{d}\sigma}) \right] , \quad (17)$$

where  $\tilde{\epsilon}_{u\bar{d}\sigma}$  and  $\tilde{\epsilon}_{I\bar{d}\sigma}$  are the upper and lower energy bands which are given by the roots of the denominator of Eq. (16). From (17), the susceptibility is obtained in the same way as for the single-ion case. The mixing term  $t_{\bar{d}}$  (taken as a constant, t) produces a band gap<sup>16</sup> of order  $kT_G = 4t^2(1 - n_f)/D$ where D is the "s" bandwidth. In a mixed-valence compound the Fermi level must lie close to  $\epsilon_f$ .

In the former case the susceptibility per atom  $\chi_{at}$  is finite at 0 °K, of order  $\mu^2 D/t^2(1-n_f)$ , and for  $T > T_G$  decreases in a Curie-Weiss way. As a specific example, the value of the  $0^{\circ}$ K susceptibility as a function of the Fermi-level position is plotted in Fig. 3 for the case of an "s" band with a constant density of states  $D^{-1}$  per atom and for the *f* level at an energy  $\epsilon_f = 0.4D$  above the bottom of the band. In actuality, the Fermi level is expected to be in the gap so the system can take advantage of the very high density of states and minimize the total energy. In this case the susceptibility vanishes at  $0^{\circ}$ K, increases up to a maximum for  $T \sim T_G$  and becomes Curie-Weiss like for  $T \gg T_G$ . Figure 4 shows a typical plot of  $\chi_{at}(T)$ for the values  $4t^2(1-n_f)/D^2 = 0.004$ ,  $\epsilon_f/D = 0.5$ , and  $\zeta = \epsilon_f$ . There is no evidence that the spin susceptibility vanishes in any of the mixed-valence compounds. However the specimens have invariably a sizeable fraction  $(\sim 10^{-3})$  of impurities and it is plausible that the gap is smeared out with a resulting finite susceptibility at 0  $^\circ K.$   $^{16}$ 

## **IV. DISCUSSION**

In summary, by constructing a strongly correlated solution to the Anderson Hamiltonian we have shown that when the position of the f level is close to the Fermi energy the susceptibility of the felectron stays finite at low temperatures and behaves as  $(T + T_G)^{-1}$  only when T is larger than a characteristic temperature determined by the

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strength of the *s*-*f* mixing interaction. We do not make quantitative comparison with experiments here because in the case of the Yb compounds the calculation requires extension to  $J = \frac{7}{2}$ , and in the case of Sm it requires taking the many-electron coupling in the Sm<sup>2+</sup> and Sm<sup>3+</sup> ions into account. A value of the order of  $v \simeq 0.1$  eV for the mixing matrix element is consistent with the experimental values.

If we calculate the excess specific heat in a similar model, we expect it, in analogy with calculations of the single impurity, to be proportional to  $T/(t^2/D)$  for  $T \rightarrow 0$  and to start decreasing at above  $T \simeq t^2/D$ . The magnitude of the low-temperature specific heat in SmB<sup>3</sup><sub>6</sub> and SmS under pressure <sup>17</sup> is such that the parameter  $t^2/D$  is consistent with that deduced from the magnetic susceptibility by this theory.

It is noteworthy that in the limit  $T \rightarrow 0$ , the interacting f band acquires all the properties of a Fermi liquid. For the case of the single-impurity problem, it is now understood that as  $T \rightarrow 0$ , the problem renormalizes <sup>18</sup> to the strong-coupling problem and the properties of the system are just those of a Fermi liquid as  $T \rightarrow 0$ . <sup>19</sup> Similar renormalizations seem to be operative in the f-band situation.

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ionic configuration are magnetic. This case will be studied separately.