Paramagnon picture of the low-temperature susceptibility of some intermediate-valence compounds

M. T. Béal-Monod* and J. M. Lawrence
Physics Department, University of California, Irvine, California 92717
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We show that the low-temperature susceptibility of $Ce(In, Sn)_3$ compounds has a quadratic temperature dependence with positive coefficient. We demonstrate that this behavior is well accounted for by a generalization to arbitrary band shapes of the paramagnon theory, which has been applied previously to liquid ^3He. This result is relevant to the whole class of mixed-valence materials. We conclude that the previously proposed phenomenology that treats valence-fluctuation materials as heavy, nearly magnetic Fermi liquids finds further support in the present analysis.

I. INTRODUCTION

Intermediate-valence compounds have been extensively studied[1] in the past few years, both experimentally and theoretically. We will confine ourselves here to those compounds which do not order at low temperature, and more particularly to $CeIn_{3-x}Sn_x$ for $x > 0.4$, for which the temperature dependence of the spin susceptibility has been recently measured[2,3] over an extended temperature range and several values of x between 0 and 3. Varma[4] has stressed that the ground-state properties of mixed-valence materials are those of a nearly magnetic Fermi liquid. This is confirmed by experiments which demonstrate the enhanced T^2 dependence of the electrical resistivity,[5] the linear temperature dependence γT of the specific heat with large values of γ,[4,5] as well as the linear variation with T of the thermal expansion,[6] and a temperature dependence of the susceptibility[2-5] resembling that of certain nearly magnetic itinerant paramagnets like Pd,[7] with a maximum followed at lower temperatures by an almost temperature-independent plateau. In all these properties, a characteristic temperature was shown to play an important role quite similar to the spin-fluctuation temperature T_{sf} of nearly magnetic fermion systems. These are described, in the paramagnon model,[8,9] by itinerant fermions interacting via a strong, contact repulsion I between opposite spins and where T_{sf} measures a Fermi temperature renormalized by the interactions, $T_{sf} = T_F(1 - \bar{I})$. [$T_F$ is the Fermi temperature in absence of interaction, and $\bar{I}$ the dimensionless interaction $IN(E_F) \propto I/E_F$, where $N(E_F)$ is the density of states at the Fermi level.]

For $CeIn_{3-x}Sn_x$ it was shown in Ref. 2 that the effective moment $\mu^2 = T\chi/C$ (where the susceptibility χ was measured for several values of x) exhibits a thermal variation which to a few percent is only a function of $T/T_{sf}(x)$. This approximate scaling appeared all the more amazing in that it held over the whole temperature range. A similar approximate scaling result has been observed in the archetypal Fermi liquid, ^3He, where T_{sf} is varied by changing the pressure.[10] This similarity lends further credence to the point of view that the magnetic properties of the intermetallics are those of a Fermi liquid.

In the present paper, we would like to present another striking feature of the $Ce(In, Sn)_3$ compounds which pleads again in favor of the spin-fluctuation description. It is not our purpose to argue on the profound significance of the paramagnon model as applied to intermediate-valence compounds, aside from some remarks; it has been stressed elsewhere[4] that the real theoretical difficulty in mixed-valence physics is to demonstrate that the behavior of the underlying microscopic Hamiltonian reduces to that of a Fermi liquid. We adopt this as a starting point and take for granted the suggestion[4] that, from a phenomenological point of view, a Fermi-liquid picture with enhanced spin fluctuations could account for magnetic properties of intermediate-valence compounds, and we take for granted the experimentally demonstrated existence of the temperature T_{sf}; what we will show is that, generally speaking, the very low-temperature susceptibility of a nearly magnetic fermion system varies like

$$\chi(T) = \chi(0)\left[1 + a\left(\frac{T}{T_{sf}}\right)^2\right] \quad \text{for } T \ll T_{sf} , \tag{1a}$$

with

$$\chi(0) \propto \frac{1}{T_{sf}} \tag{1b}$$

and a is a number of order 1, which can be negative or positive. Such a behavior follows from a generalization to an arbitrary band shape of the paramagnon result[9] derived for liquid ^3He with one parabolic band of fermions with a spherical Fermi surface. In the

^{3}He case the coefficient a was negative, so that the susceptibility decreased for increasing temperatures in excellent agreement with experiments[9,10]; the fit was all the more remarkable in that the theoretical result contained no adjustable parameter. We will show that formula (1) is quite general for nearly magnetic systems and that the coefficient a and its sign depend only on the values and signs of the first few derivatives of the density of states at the Fermi level. Thus at low temperatures ($T \ll T_{sf}$) $\chi(T)$ can be either monotone decreasing with increasing temperature ($a<0$) as in ^{3}He, or monotone increasing ($a>0$). If the latter holds, then, since at high temperatures ($T \gg T_{sf}$) the susceptibility decreases in a Curie-Weiss fashion, there must be a maximum of $\chi(T)$ at an intermediate temperature.

It has been argued on general grounds that band-structure effects can cause the T^2 term in $\chi(T)$ to take a positive sign.[11] Certain authors[12,13] argued that the maximum observed in $\chi(T)$ for several nearly magnetic systems was due to a $T^2 \ln T$ variation in $\chi(T)$; but this was shown to be erroneous[14,15] because, although such $T^2 \ln T$ terms exist, when they are carefully collected, they altogether cancel, and the only surviving term is the T^2 term. The latter was derived in Ref. 9 from first principles (by differentiating the free energy with respect to the field).

Once we have derived Eq. (1) in Sec. II we will compare it in Sec. III to the experimental data for $CeIn_{3-x}Sn_x$. To accomplish this we rewrite Eq. (1) in the form

$$\chi(T)=\chi(0)\{1+b[\chi(0)T]^2\} \ . \tag{2}$$

Such a form has been shown valid for liquid ^{3}He.[9,10] Therefore if the data for $\chi(T)$ plotted versus T^2 exhibit linear behavior, the extrapolated intercept gives $\chi(0)$ and the slope gives the coefficient b which can then be compared to the theory. To accomplish this we first show that one can subtract with quite good precision the spurious impurity term responsible for an extra $1/T$ contribution at the lowest temperatures. What remains fits the above formula very well, i.e., varies linearly with $[\chi(0)T]^2$. In the ensuing discussion we compare the data of $Ce(In, Sn)_3$ to that of liquid ^{3}He bringing out similarities and differences between the two cases.

II. EXTENSION TO AN ARBITRARY BAND SHAPE OF THE PARAMAGNON SUSCEPTIBILITY OF A NEARLY MAGNETIC FERMI LIQUID

In this section we will generalize the result obtained in Ref. 9 for the temperature dependence of the susceptibility of strongly interacting fermions in the paramagnon model. The theory is extended so as to apply to a band of itinerant fermions of arbitrary shape, in contrast with the parabolic band appropriate to liquid ^{3}He and considered in Ref. 9.

A. General formulas

As in Ref. 9 we first compute the irreducible two-particle dynamic susceptibility $\tilde{\chi}^0(q,\omega,T)$, which includes fluctuation effects arising from the emission and reabsorption of spin fluctuations (paramagnons) by the fermion propagators; then the dynamic susceptibility in the presence of an interaction, $\chi(q,\omega,T)$, is computed in random phase approximation (RPA)

$$\chi(q,\omega,T)=\frac{\tilde{\chi}^0(q,\omega T)}{1-I\tilde{\chi}^0(q,\omega,T)} \ . \tag{3}$$

The static susceptibility then follows from the $\omega=0$, $q=0$ limit:

$$\chi(T)\equiv\chi(0,0,T)=\frac{\tilde{\chi}^0(0,0,T)}{1-I\tilde{\chi}^0(0,0,T)} \equiv\frac{\tilde{\chi}^0(T)}{1-I\tilde{\chi}^0(T)} \ . \tag{4}$$

For a system close to a ferromagnetic instability the susceptibility is maximum for $q=0$; and $\bar{I}\equiv IN(E_F) \lesssim 1$ so that for $T_{sf}=(1-\bar{I})T_F$ it follows that $T_{sf} \ll T_F$. For $T \ll T_{sf}$ the fluctuation effects are treated as perturbations in powers of T/T_{sf}, modifying the bare temperature-dependent Pauli susceptibility $\chi^0(T)$ to $\tilde{\chi}^0(T)$ where

$$\tilde{\chi}^0(T)=\chi^0(T)[1+\delta\chi_{fl}(T)] \ . \tag{5}$$

As is well known the temperature dependence of the Pauli susceptibility is obtained through a Sommerfeld expansion in powers of T/T_F

$$\chi^0(T)=\chi^0(0)[1+\delta\chi^0(T)] \ . \tag{6}$$

$\chi^0(0)$ is determined by the density of states at the Fermi level evaluated at $T=0$ so that, in appropriate units

$$\chi^0(0)=N(E_F) \ , \tag{7a}$$

$$\delta\chi^0(T)=\tfrac{1}{6}\pi^2T^2\left[\frac{N''}{N}-\frac{N'^2}{N^2}\right]_{E_F} \ , \tag{7b}$$

where N' and N'' are the first and second derivatives of N evaluated at E_F.

Collecting Eqs. (4)–(6) we then have

$$\chi(T)\cong\frac{\chi^0(0)}{1-\bar{I}}\left[1+\frac{1}{1-\bar{I}}[\delta\chi^0(T)+\delta\chi_{fl}(T)]\right] \ . \tag{8}$$

This last formula is quite general and useful, and it clearly separates the fluctuation contribution. We first show that it leads to known results in the appropriate limits. (i) In the absence of interaction

$I=0$ and, *a fortiori*, $\delta\chi_{fl}=0$, so that

$$\chi(T)\rightarrow\chi^0(0)[1+\delta\chi^0(T)]$$
$$=N(E_F)\left[1+\left(\frac{N''}{N}-\frac{N'^2}{N^2}\right)_{E_F}\frac{\pi^2}{6}T^2\right] , \quad (9)$$

which for a parabolic band leads back to the temperature dependence of the Pauli susceptibility

$$\chi_{\text{Pauli}}=N(E_F)\left[1-\tfrac{1}{12}\pi^2\left(\frac{T}{T_F}\right)^2\right] . \quad (10)$$

(ii) If fluctuation effects are neglected $\delta\chi_{fl}=0$ then, for finite I we recover the Stoner susceptibility

$$\chi(T)\rightarrow\frac{\chi^0(0)}{1-\bar{I}}\left[1+\frac{1}{1-\bar{I}}\delta\chi^0(T)\right]$$
$$=\frac{\chi^0(0)}{1-\bar{I}}\left[1+\frac{1}{1-\bar{I}}\left(\frac{N''}{N}-\frac{N'^2}{N^2}\right)_{E_F}\frac{\pi^2}{6}T^2\right] , \quad (11)$$

where, for a parabolic band

$$\chi_{\text{Stoner}}=\frac{N(E_F)}{1-\bar{I}}\left[1-\tfrac{1}{12}\pi^2\frac{T^2}{(1-\bar{I})T_F^2}\right] . \quad (12)$$

Note that only one power of $1/(1-\bar{I})$ enters into the coefficient of T^2. (iii) In the presence of fluctuation effects, we will show in Sec. II B that

$$\delta\chi_{fl}=F\left(\frac{N''}{N},\frac{N'}{N}\right)_{E_F}\frac{T^2}{1-\bar{I}} , \quad (13)$$

where F is a function of N, N', and N'' which when evaluated at E_F can be positive or negative, depending only on the band shape at the Fermi level. Then, assuming that F is finite at E_F, and close to a ferromagnetic instability ($\bar{I}\sim 1$), $\delta\chi^0(T)$ will be negligible compared to $\delta\chi_{fl}$, and one obtains:

$$\chi(T)=\frac{\chi^0(0)}{1-\bar{I}}\left[1+\frac{1}{1-\bar{I}}\delta\chi_{fl}\right]$$
$$=\frac{\chi^0(0)}{1-\bar{I}}\left[1+F\left(\frac{N''}{N},\frac{N'}{N}\right)_{E_F}\frac{T^2}{(1-\bar{I})^2}\right] . \quad (14)$$

Note that $1/(1-\bar{I})$ appears to the power 2 in the coefficient of T^2: one power comes from the mean-field hypothesis of Eq. (3) and was already present in the Stoner result of formula (12); the extra power comes from the fluctuation effects renormalizing $\tilde{\chi}^0$. Then since, by definition

$$T_{sf}=(1-\bar{I})T_F \quad (15)$$

and since

$$\chi(T=0)=\frac{\chi^0(0)}{1-\bar{I}}=\frac{N(E_F)}{1-\bar{I}}=\frac{\lambda}{T_{sf}} , \quad (16)$$

where λ is a constant, one can write Eq. (14)

$$\chi(T)=\chi(0)\left[1+T_F^2F\left(\frac{N''}{N},\frac{N'}{N}\right)_{E_F}\frac{T^2}{T_{sf}^2}\right] \quad (17a)$$

or, equivalently

$$\chi(T)=\chi(0)\left[1+\frac{T_F^2}{\lambda^2}F\left(\frac{N''}{N},\frac{N'}{N}\right)_{E_F}[\chi(0)T]^2\right] . \quad (17b)$$

Equations (17a) and (17b) are identical to the forms (1a) and (2), respectively. For the parabolic band of liquid ^{3}He studied in Ref. 9, F was computed and reduced to

$$F=-3.2\pi^2/24T_F^2 \quad (18)$$

yielding for the low-temperature dependence of the spin susceptibility of liquid ^{3}He the paramagnon result[9]

$$\chi(T)=\frac{N(E_F)}{1-\bar{I}}\left[1-\frac{3.2\pi^2}{24}\frac{T^2}{(1-\bar{I})^2T_F^2}\right] , \quad (19)$$

which takes the form (1a) with $a<0$ for a parabolic band. Then

$$T\chi(T)=\lambda\frac{T}{T_{sf}}\left[1-\frac{3.2\pi^2}{24}\frac{T^2}{T_{sf}^2}\right] \quad (20)$$

clearly exhibiting the dependence on the reduced temperature T/T_{sf}. One can write equivalently

$$T\chi(T)=T\chi(T=0)\left[1-\frac{3.2\pi^2}{24}[\tfrac{2}{3}\chi(T=0)]^2T^2\right] , \quad (21)$$

which has the form of formula (2) with $b<0$. This last formula appeared in Ref. 9 as formula (21).

According to Eq. (13) $\delta\chi_{fl}$ vanishes at $T=0$, and diverges as $\bar{I}\rightarrow 1$. Actually $\delta\chi_{fl}$ contains a temperature-independent term $\delta\chi_{fl}(T=0)$, but this term does not diverge as $\bar{I}\rightarrow 1$, as will become clear in Sec. II B. Hence strictly speaking, according to Eqs. (4) and (5)

$$\chi(0)=\frac{\chi^0(0)[1+\delta\chi_{fl}(0)]}{1-\bar{I}\chi^0(0)[1+\delta\chi_{fl}(0)]} . \quad (22)$$

Clearly the additional term can be absorbed into $\chi^0(0)$, leading to an effective interaction $\bar{I}_{\text{eff}}=I[1+\delta\chi_{fl}(0)]$. It was shown in Ref. 16 that due to quantum effects at $T=0$ K, the effective spatial dimensionality of the three-dimensional paramagnon model is 6. This is larger than the upper marginal dimensionality $d^*=4$, defined such that for $d>d^*$ mean-field theory is valid arbitrarily close to the critical point. In other words $\chi(0)\propto 1/(1-\bar{I}_{\text{eff}})^\gamma$ with $\gamma=1$ and $\bar{I}_{\text{eff}}$ may be calculated in perturbation theory. In Ref. 17 an attempt was made to calculate χ and $\bar{I}_{\text{eff}}$ self-consistently, but the calcula-

tion is not tractable analytically. In the present paper (as well as in Ref. 9) $\chi(0)$ will be extracted from experimental data; therefore we ignore $\delta\chi_{\text{fl}}(0)$ in the following, since it is incorporated into the measured value.

B. Derivation of $\delta\chi_{\text{fl}}(T)$

In Ref. 9, which was concerned with liquid ^{3}He, the susceptibility was derived by differentiation of the free energy with respect to the magnetic field. Such a procedure would be very difficult for a nonparabolic band. However, diagrammatically this procedure amounts to dressing the bare bubble $\chi^0(q,\omega)$ with paramagnon insertions in all possible ways. To lowest order we need to compute the five diagrams of Fig. 4 in Ref. 18 involving one paramagnon insertion in all possible ways; this procedure will then yield Eq. (13) above. These five diagrams are (in the order of their appearance in Fig. 4, Ref. 18):

(i) A self-energy correction containing an odd number of rings with the propagator

$$\frac{-I^2\chi^0(q,\omega)}{1-I^2[\chi^0(q,\omega)]^2} \quad . \tag{23a}$$

(ii) A self-energy correction involving a ladder diagram, with the propagator

$$\frac{-I^2\chi^0(q,\omega)}{1-I\chi^0(q,\omega)} \quad . \tag{23b}$$

Here $\chi^0(q,\omega)$ is computed at 0 K, as will be seen to be sufficient later on; q and ω are the fluctuation momentum and energy transfers. The most important fluctuations have $q,\ \omega\to 0$. Equations (23) have to be multiplied by a factor of 2 to take account of the symmetric diagram.

(iii) A vertex correction involving an even number of rings with propagator

$$\frac{I^3[\chi^0(q,\omega)]^2}{1-I^2[\chi^0(q,\omega)]^2} \quad . \tag{23c}$$

(iv) A pair of diagrams which appear to involve two paramagnon insertions rather than one, but which when combined are of the same order as the other three

$$\left[\frac{I}{1-I\chi^0(q,\omega)}\right]\left[\frac{I^2\chi^0(q,\omega)}{1-I^2[\chi^0(q,\omega)]^2}\right] + \left[\frac{-I}{1-I\chi^0(q,\omega)}\right]\left[\frac{I}{1-I^2[\chi^0(q,\omega)]^2}\right] = \frac{-I^2}{1-I^2[\chi^0(q,\omega)]^2} \quad . \tag{23d}$$

(This again has to be multiplied by 2, for the same symmetry reason as above.) The physical meaning of the combination was expained in Ref. 19. Essentially, in a rotational invariant formulation, only one spin fluctuation appears in these two diagrams; the other being a density fluctuation of the form $1/[1+I\chi^0(q,\omega)]$ which has no divergence for $q,\ \omega\to 0$ and $\bar{I}\to 1$.

The q and ω fluctuation transfers also appear in the fermion propagators in these diagrams and were taken account of in both Refs. 9 and 18, but the resulting analytical calculation was very lengthy. In the present case for arbitrary band shape, it would be even messier. Since our purpose is essentially only to extract the T^2 dependence of Eq. (13) and show that the coefficient F can be positive as well as negative depending on the band shape, we will neglect the q and ω transfers in all the fermion propagators in the computation of the above five diagrams; the error introduced will affect the coefficient of the T^2 term by a numerical factor but will not affect the characteristic features exhibited in Eq. (13). Then, the task is considerably simplified; for $\bar{I}$ close to 1, we are left with

$$N(E_F)\delta\chi_{\text{fl}}(T) = c\left[-\frac{5I}{2N(E_F)}T\sum_{k,\epsilon}G_0^4(k,\epsilon) - \frac{I}{N^2(E_F)}\left[T\sum_{k,\epsilon}G_0^3(k,\epsilon)\right]^2\right]T\sum_{q,\omega}\frac{\chi^0(q,\omega)}{1-I\chi^0(q,\omega)} \quad . \tag{24}$$

As in Refs. 9 and 18, $\bar{I}$ is set equal to 1 whenever it does not appear in a divergent quantity; c is a constant which accounts for the numerical error due to the above approximation. One then has

$$T\sum_{k,\epsilon}G_0^4(k,\epsilon) = \frac{-1}{3!}N''(E_F) \quad , \tag{25}$$

$$T\sum_{k,\epsilon}G_0^3(k,\epsilon) = \frac{1}{2!}N'(E_F) \quad , \tag{26}$$

and (see the Appendix)

$$T\sum_{q,\omega}\frac{\chi^0(q,\omega)}{1-I\chi^0(q,\omega)} \propto [N(E_F)]^2\pi^2\frac{T^2}{1-\bar{I}} \quad . \tag{27}$$

Therefore

$$\delta\chi_{\text{fl}}(T) \propto \left[\frac{5}{2(3!)}\frac{N''}{N} - \frac{1}{4}\left[\frac{N'}{N}\right]^2\right]_{E_F}\pi^2\frac{T^2}{1-\bar{I}} \tag{28}$$

and then Eq. (19) becomes

$$\chi(T) = \chi(T=0)\left\{1 + c_0\pi^2\frac{T^2}{(1-\bar{I})^2}\times\left[\frac{5}{12}\frac{N''}{N} - \frac{1}{4}\left[\frac{N'}{N}\right]^2\right]_{E_F}\right\} \tag{29a}$$

or

$$\chi(T)=\chi(T=0)\left[1+c_0\pi^2T_F^2\left(\frac{5}{12}\frac{N''}{N}-\frac{1}{4}\frac{N'^2}{N^2}\right)_{E_F}\frac{T^2}{T_{sf}^2}\right] . \tag{29b}$$

Here c_0 accounts both for the constant c and for the proportionality coefficient in Eq. (27). For a parabolic band (29) would give

$$\chi(T)=\chi(T=0)\left[1-c_0\frac{\pi^2}{6}\frac{T^2}{(1-\bar{I})^2T_F^2}\right] , \tag{30}$$

which, compared with the complete result (19) of Ref. 9, shows that the numerical coefficient c_0 is of order 1 (equal to 3.2/4 in that case). Therefore, in Eq. (1a)

$$a=c_0\pi^2T_F^2\left(\frac{5}{12}\frac{N''}{N}-\frac{1}{4}\frac{N'^2}{N^2}\right)_{E_F} . \tag{31}$$

C. Discussion

Formula (29) clearly exhibits the conditions under which $\chi(T)$ will initially decrease or increase as T increases, and hence the conditions under which a maximum is expected in the temperature variation of $\chi(T)$. (i) If $N''(E_F)<0$, $\chi(T)$ will decrease continuously as T increases and there will be no maximum. This would hold for any material, such as ^{3}He, where the band is parabolic. (ii) If $N''(E_F)>0$ but $N''/N<\frac{3}{5}N'^2/N^2$ then the same behavior would occur as in (i). (iii) If $N''(E_F)>0$ and $N''/N>\frac{3}{5}N'^2/N^2$ then, on the contrary, χ will initially increase with T as T^2, and a maximum should be observed. For example, for a Lorentzian density of states with half width Γ and center E_f, this condition would hold whenever $E_F-E_f>(5/9)^{1/2}\Gamma$; if E_f represented the position of the $4f$ level, this condition would be satisfied when the level is nearly fully occupied, i.e., for a nearly integral valence material.

In the derivation of Eq. (29) we have assumed that the Fermi liquid is nearly ferromagnetic. However, the ordering which occurs in $CeIn_3$ is at finite $\vec{q}$; i.e., it orders antiferromagnetically.[2] This does not necessarily imply that those compounds which do not order, e.g., the tin-rich $Ce(In, Sn)_3$ compounds, should be treated in the phenomenology as nearly antiferromagnetic. Nevertheless we wish to consider this issue briefly. For nearly antiferromagnetic materials the mean-field susceptibility diverges for finite $\vec{q}=\vec{q}_0$. It follows[20] that for small $\vec{q}-\vec{q}_0$ and small ω one can expand $\chi^0(q,\omega)$ around its maximum, in analogy to Eq. (A4), but the coefficients of ω and ω^2 no longer have the long-wavelength divergence. The upshot should be that the coefficient of the T^2 term, although enhanced by the spin fluctuations, should not increase as dramatically as $T_{sf}\to 0$ as in the nearly ferromagnetic case except for very particular Fermi surfaces.[20] We hope to consider this more carefully in the future.

In the event that the Stoner enhancement is not large, the Pauli contribution $\delta\chi^0(T)$ [which we neglected in the derivation of Eq. (29)] is expected to contribute to the T^2 term. As can be seen from Eq. (7b), there exists a set of conditions similar to (i) through (iii) under which the resulting coefficient will be positive or negative.

We wish to cite here the work of Ref. 21 which accounts for arbitrary band shape, for the temperature dependence of χ^0 and also for I, but does not include the fluctuation contribution $\delta\chi_{fl}$. This amounts to computing Eq. (11) with a temperature-dependent interaction; i.e., it results in a Stoner-type formula where the interaction varies with T. It seems very unlikely that this could account even phenomenologically for the various paramagnon insertions that we consider here.

III. VERIFICATION OF T^2 BEHAVIOR IN THE SPIN-FLUCTUATION ALLOY SYSTEM $CeIn_{3-x}Sn_x$

A. Experimental results

As an example of a metallic spin-fluctuation system we consider the alloys $CeIn_{3-x}Sn_x$ (Ref. 2) which exhibit a continuous valence transition from trivalence ($x<2.3$) to weakly nonintegral valence for $x>2.3$. For all samples with $x>0.4$ the ground state is nonmagnetic. The susceptibility of three representative samples (the data taken from Ref. 2) is shown in Fig. I. At high temperatures the susceptibility is Curie-Weiss-like

$$\chi(x;T)=C/[T+\Theta(x)] , \tag{32}$$

where $C=0.807$ emu K/mole is the Curie constant for free $J=\frac{5}{2}$ cerium moments. At a temperature $T_{max}\simeq\frac{1}{2}\Theta$ there is a broad maximum in the susceptibility, and at low temperatures the susceptibililty tends to the constant value

$$\chi(x;0)\simeq C/2\Theta(x) . \tag{33}$$

(This constancy is obscured by the presence of an impurity contribution, to be discussed in detail below.) As discussed in Ref. 2 we take the Curie-Weiss parameter as a measure of the characteristic temperature for spin fluctuations; i.e., $T_{sf}(x)=\Theta(x)$. The values of $T_{sf}(x)$ for the samples discussed in this paper are given in Table I, where it can be seen that $T_{sf}(x)$ varies by a factor of 3.

We now consider the low-temperature behavior more carefully. At the lowest temperatures the susceptibility rises with decreasing temperature. The

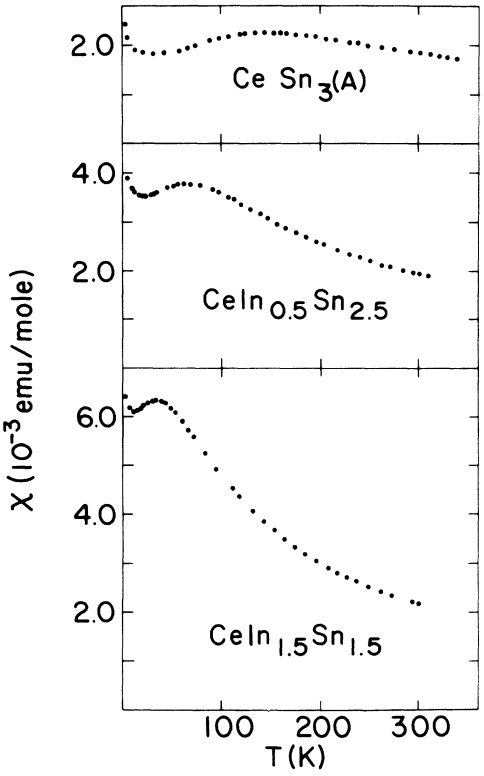

FIG. 1. Susceptibility vs temperature for three samples of $CeIn_{3-x}Sn_x$; the data are from Ref. 2.

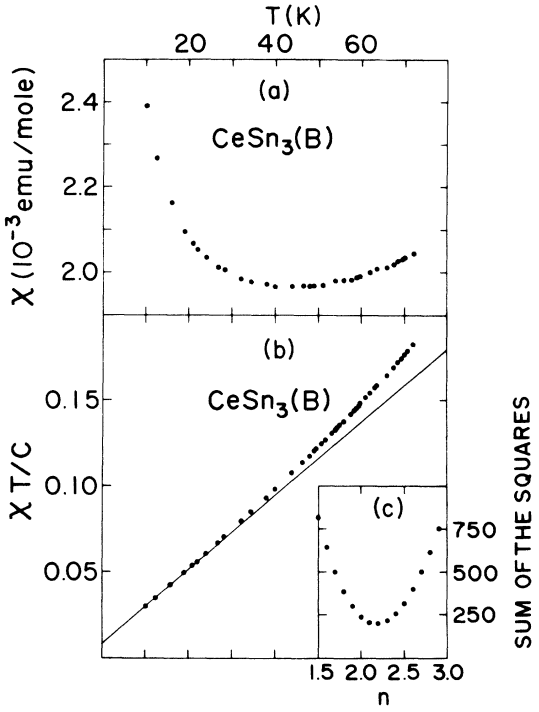

Fig. 2. (a) Low-temperature susceptibility for a second sample of $CeSn_3(B)$. (b) $\chi T/C$ vs T for $CeSn_3(B)$. C is the cerium $J=\frac{5}{2}$ free-ion Curie constant. The solid line represents the behavior $C_{imp}/C + T\chi(0)/C$, where the values of C_{imp} and $\chi(0)$ are taken from Table I. This asymptotic linear behavior at low temperature supports the assumption that the impurities contribute to the susceptibility simply as C_{imp}/T. (c) Sum of the squares of the residuals vs exponent n for a least-squares fit of the data for $CeSn_3(B)$ to the equation $\chi(T)=\chi(0)+AT^n+C_{imp}/T$. The data set included 41 points in the interval 10–72 K. The minimum near $n=2$ demonstrates the low-temperature T^2 behavior.

magnitude of the rise varies for two samples of the same composition, and is also markedly affected by annealing. Hence, the rise is not intrinsic, but is an extrinsic effect due to foreign impurities, oxides of cerium, etc.[2,3] At still higher temperatures (e.g., 30–80 K in $CeSn_3$) the susceptibility increases with T and is concave upward; it is for this region that the T^2 behavior is most clearly present, as we shall show.

To demonstrate convincingly the T^2 law, we have improved on the statistics of the data of Ref. 2 by making a new sample $CeSn_3(B)$, and measuring its susceptibility between 10 and 80 K. The results are shown in Fig. 2(a). There is clearly a region where χ increases with T faster than linearly; but it is also clear that proper account of the impurity contribution must be made before the power law can be established.

To accomplish this we argue that the simplest assumption concerning the impurity behavior is that it

TABLE I. Valence Z, spin-fluctuation temperature T_{sf}, impurity Curie constant, intrinsic zero-temperature susceptibility, and coefficient of the T^2 term for four samples of $CeIn_{3-x}Sn_x$. The values of C_{imp}, $\chi(0)$, A, and β are taken from least-squares fits of the data to $\chi(T)=\chi(0)+AT^2+C_{imp}/T=\chi(0)\{1+\beta[\chi(0)/C]^2T^2\}+C_{imp}/T$.

Sample	Z	T_{sf} (K)	C_{imp} (10^{-6} emu K/mole)	$\chi(0)$ (10^{-6} emu/mole)	A (10^{-6} emu/mole K^2)	β (K^{-2})
$CeSn_3(A)$	3.1	$\gtrsim$200	2290	1713	0.042	5.4
$CeSn_3(B)$	3.1	$\gtrsim$200	6449	1742	0.041	5.0
$CeIn_{0.5}Sn_{2.5}$	3.0+	120	3400	3281	0.19	3.4
$CeIn_{1.5}Sn_{1.5}$	3.0	70	1479	5885	0.67	2.1

is of the form C_{imp}/T. While other forms are plausible (e.g., the impurity may experience crystal-field effects) this assumption is nevertheless quite reasonable, and as we will show below, there are important self-consistency checks supporting it.[22] Thus we assume that the low-temperature behavior of the measured susceptibility is related to the intrinsic susceptibility by

$$\chi_{meas}(T) = \chi_{int}(T) + (C_{imp}/T) \tag{34}$$

$$= \chi(0) + AT^n + (C_{imp}/T) \ , \tag{35}$$

where $\chi(0)$, A, n, and C_{imp} are to be determined from the data.

As a first self-consistency check we plot in Fig. 2(b) the quantity $T\chi_{meas}/C$ which we expect to approach $T=0$ linearly with slope $\chi(0)/C$ and intercept C_{imp}/C; at high temperatures it should rise faster than linearly. All these features are apparent in Fig. 2(b), giving firm support to our assumption.

Next, for various choices of exponent n we performed least-squares fits to the data of $CeSn_3(B)$ with $\chi(0)$, A, and C_{imp} as parameters of the fit. In Fig. 2(c) we plot the sum of the squares versus the value of the exponent n; it is seen to have a well-defined minimum at $n \approx 2.15$. This is sufficiently close to the value $n=2$ that we assert that the true behavior is as T^2. [Several factors would cause this small deviation from the value $n=2$; (a) the thermal lag effects discussed in Ref. 2; (b) incorrect choice of the fitting interval, e.g., for 29 data points in the interval 10–60 K the optimal value of n was 1.90.]

As a final demonstration of the T^2 behavior we exhibit in Fig. 3 plots of the intrinsic susceptibility $\chi_{int}(T)$ vs T^2, where C_{imp} is taken from the least-squares fit to Eq. (35) when the exponent is constrained to the value $n=2$. The data for $CeSn_3(B)$ give especially striking confirmation of the T^2 behavior. The values of C_{imp}, $\chi(0)$, and A are listed in Table I. As a second self-consistency check on our subtraction of impurity background, we note that the values of $\chi(0)$ and A (i.e., the intrinsic susceptibility) are in good agreement for the two samples of $CeSn_3$ even though the impurity contributions differ by a factor of 3.

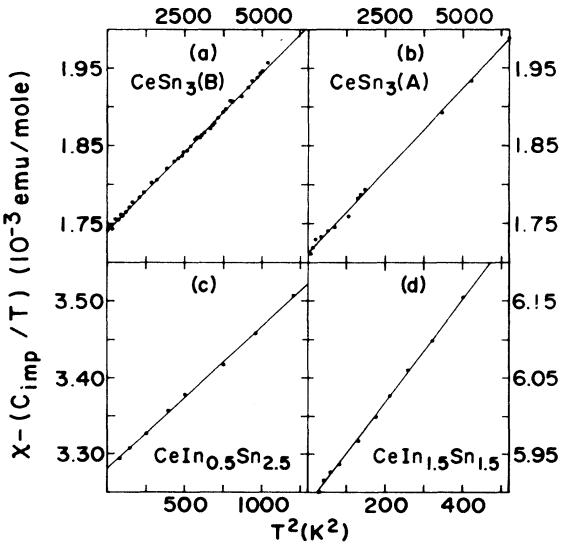

FIG. 3. Intrinsic susceptibility $\chi_{meas} - C_{imp}/T$ vs T^2 for all four samples of $CeIn_{3-x}Sn_x$. The solid lines represent the best fits to $\chi(0) + AT^2$, where the values of $\chi(0)$, A, and C_{imp} are taken from Table I.

To make further comparison with the theory, we write

$$\chi(T) = \chi(0)[1 + a(T/T_{sf})^2] \tag{36}$$

$$= \chi(0)\{1 + \beta[\chi(0)/C]^2T^2\} \ , \tag{37}$$

where we have assumed $T_{sf} \simeq C/2\chi(0)$ as mentioned above, and where $A = \beta\chi^3(0)/C^2$ and $a \approx \frac{1}{4}\beta$. The values of the constant β are listed in Table I; while they vary somewhat with x, all values observed are of the same order of magnitude, namely, of order unity.

B. Discussion of the low-temperature behavior of $CeIn_{3-x}Sn_x$ and comparison with that of liquid ^3He

We thus see that the low-temperature susceptibility for $CeIn_{3-x}Sn_x$ is adequately represented by Eq. (1) or (2). This gives strong support to the Fermi-liquid picture. Stated in even greater generality, the existence of a T^2 term in the susceptibility, with its innuendo of a Sommerfeld expansion, attests to the fermion character of the $4f$ electrons in the ground state. This obedience to quantum statistics (as opposed to the classical statistics obeyed by conventional rare-earth materials) is a hallmark of the intermediate-valence ground state.

The coefficient of the T^2 term for $CeIn_{3-x}Sn_x$ is positive; hence, if these intermetallics can be described by the theory outlined in Sec. II, it follows from Eq. (29) that the conditions $N''/N > \frac{3}{5}(N'^2/N^2)|_{E_F}$ and $N''(E_F) > 0$ must be satisfied. As we noted in Sec. IIC if we model the $4f$ band by a Lorentzian centered at E_f and with width Γ these conditons are satisfied for $E_F - E_f > (\frac{5}{9})^{1/2}\Gamma$; this occurs for nearly complete occupancy of the level, i.e., for nearly integral valence. This condition is indeed satisfied in $CeI_{3-x}Sn_x$; the alloys are essentially trivalent for $x < 2.3$; the valence increases smoothly with x in the interval $2.3 < x < 3.0$ to the value 3.1 for $CeSn_3$ (Table I). We are suggesting that the positive coefficient, and hence the susceptibility maximum, are associated with the near integral valence of the material and would not be expected were the Fermi level pinned to the peak of the $4f$ band (strong intermediate valence), since in the latter case we would have $N''(E_F) < 0$ so that the condition (i) of Sec. IIC would be satisfied. Indeed, the transition

metal palladium, which exhibits a susceptibility maximum, also satisfies this condition that the Fermi level is very near the top of the band[21]

Given that the observed T^2 behavior in Ce(In, Sn)$_3$ represents a form of Fermi-liquid behavior, it behooves us to make a more detailed comparison to the behavior of that archetypal Fermi liquid, ^{3}He. In Ref. 10 it was found that Eq. (37) is obeyed for ^{3}He, with β negative and of magnitude 0.53; this is in excellent agreement with the paramagnon value 0.58. Furthermore β remained constant as the pressure was varied, while $\chi(0)$ and hence T_{sf} varied by a factor of 2. This latter represents scaling behavior; i.e., as long as the coefficient a in Eq. (1a) does not vary with $\chi(0)$, the "effective moment" $T\chi(T)$ is a function only of a scale variable $\tau = T/T_{sf}$. This is demonstrated in Fig. 4 of Ref. 10.

From Table I it is seen that as x varies in $CeIn_{3-x}Sn_x$ causing $\chi(0)$ to vary by a factor of 3.4, the coefficient β varies by a factor of 2.5. Such a variation with x is a weak effect, since the full coefficient A of the T^2 term varies as $\beta\chi^3(0)/C^2$; i.e., $\chi^3(0)$ varies by a factor of 40, on which scale the variation of β is an order of magnitude smaller. Such a weak variation of β is indeed expected to arise, given Eq. (29); i.e., one effect of varying x should be to shift the position of the Fermi level with respect to E_f, hence causing N, N', and N'' to vary; this certainly must happen since the valence changes as x increases above the value 2.3.

However, this variation implies that the scaling observed[2] in $CeIn_{3-x}Sn_x$ is only approximate at low temperatures. Since the T^2 contribution is only a small fraction of the total susceptibility, the deviation from scaling is not large. It is also not clear whether the deviation is present for all x, or only as the material becomes truly mixed valent for $x > 2.3$; in Ref. 2 it is already suggested that scaling may break down in the strong intermediate-valence regime. This situation—that at low temperatures the scaling observed in liquid ^{3}He is quite accurate, while only approximate in $CeIn_{3-x}Sn_x$—is reversed at higher temperatures. As can be seen from Fig. 5 of Ref. 10, when $\chi T/C$ for ^{3}He is plotted versus the scale variable τ marked deviations (of order 3%) are observed at high temperatures when the data for two different pressures [and hence two different $T_{sf}(P)$] are plotted simultaneously.

We stress again, however, that the deviations from scaling are in both cases quite small. It is truly a remarkable fact that the susceptibility of liquid ^{3}He approaches the classical value at temperatures of order T_{sf}, which is well below the degeneracy temperature T_F; and that it does so, to within a few precent, only as a function of a scaled temperature variable. This is not well understood theoretically for ^{3}He. That essentially the same behavior is obeyed by the susceptibility of $CeIn_{3-x}Sn_x$ strengthens the argument that these intermetallics behave as Fermi liquids—surprisingly even the high-temperature scaling ($T > T_{sf}$) may represent a Fermi-liquid property.

IV. CONCLUSION

We have seen that the phenomenological picture of intermediate-valence materials as nearly magnetic Fermi liquids goes a long way towards describing their low-temperature susceptibility. Future experiments in other systems are warranted. It would be extremely interesting, for example, to see whether the susceptibility of $CeAl_3$ obeys a T^2 law below the maximum which occurs in that system around 600 mK (Ref. 5); this is particularly attractive in that many other properties of the system[5,6] indicate that it behaves as a Fermi liquid with an unusually large enhancement.

In future extensions of the theory we intend to examine the effect on the specific heat and resistivity of arbitrary band shape. A more detailed treatment of nearly antiferromagnetic materials is also warranted. It is clear that the central issue vis-a-vis the Fermi-liquid behavior is to show how it emerges from the underlying mixed-valence Hamiltonian. Only then will it be possible to calculate the actual band shapes which enter the phenomenology.

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APPENDIX

A. Calculation of Eq. (27)

We want to calculate

$$J = T\sum_{q,\omega}\frac{\chi^0(q,\omega)}{1-I\chi^0(q,\omega)}\ , \tag{A1}$$

$$J = \frac{1}{(2\pi)^4}\int d^3q\int d\omega\left[1+\frac{2}{e^{\omega/T}-1}\right]\left[\frac{2\,\mathrm{Im}\chi^0(q,\omega)}{[1-I\,\mathrm{Re}\chi^0(q,\omega)]^2+[I\,\mathrm{Im}\chi^0(q,\omega)]^2}\right]\ , \tag{A2}$$

which can be expanded in powers of T

$$J(T) = J(T \to 0) + T^2 K(T \to 0) \quad . \tag{A3}$$

For a nearly ferromagnetic Fermi liquid, $\chi^0(q, \omega)$ has an absolute maximum for $\omega = 0$, $q = 0$; therefore for small q and ω it may be written quite generally, preserving the homogeneity of the formula and the symmetry of the Hilbert transforms, as

$$\chi^0(q, \omega) \approx N(E_F)\left(1 - \alpha\frac{q^2}{k_F^2} - \delta\frac{\omega^2}{v_F^2 q^2} + i\beta\frac{\omega}{v_F q}\right) \quad . \tag{A4}$$

The constants α, β, and δ depend on the band shape. Strictly speaking they are tensors, but we assume that they are positive scalars; this simplifies the calculation without affecting the main result, viz., the form of Eq. (27).

The divergences in powers of $1/q$ in Eq. (A4) follow from the nearly ferromagnetic character for which long wavelengths dominate (infrared divergences) in contrast with the nearly antiferromagnetic case where the coefficients of ω and ω^2 do not diverge.[20] However, the interesting region is that for which $\omega/v_F q < 1$; i.e., ω goes to zero faster than q.

We first sketch the calculation of $J(T \to 0)$ in order to show that $\delta\chi_{\text{fl}}(T = 0)$ is not a divergent quantity when $\bar{I} \to 1$, so that it can be absorbed into a redefinition of $\bar{I}$ as explained at the end of Sec. II A:

$$J(T \to 0) \propto \int_0^{q_0} q\, dq \int_0^{v_F q} \frac{\omega\, d\omega}{(1 - I\,\mathrm{Re}\chi^0)^2 + (\bar{I}\beta\omega/v_F q)^2} \tag{A5}$$

$$\propto \int_0^{q_0} q^3\, dq \ln\left[\frac{(1 - I\,\mathrm{Re}\chi^0)^2 + (\bar{I}\beta)^2}{(1 - I\,\mathrm{Re}\chi^0)^2}\right] \quad , \tag{A6}$$

where q_0 is a momentum cutoff of order k_F. When $q \to 0$ and $\bar{I} \to 1$ the integral of the numerator is clearly nondivergent; the denominator gives

$$\int_0^{q_0} q^3\, dq \ln\left[1 - \bar{I}\left[1 - \alpha\frac{q^2}{k_F^2}\right]\right] \quad , \tag{A7}$$

which has the form

$$\int_0^{q_0^2} x\, dx \ln\left[1 - \bar{I} + \frac{\bar{I}\alpha}{k_F^2}x\right] \quad , \tag{A8}$$

which remains finite when $\bar{I} \to 1$.

The calculation of K amounts to expanding the denominator of Eq. (A2) in powers of ω

$$(1 - I\,\mathrm{Re}\chi^0)^2 + (I\,\mathrm{Im}\chi^0)^2 \simeq A^2 + B^2\omega^2/v_F^2 q^2 \quad , \tag{A9}$$

where

$$A^2 = (1 - \bar{I} + \bar{I}\alpha q^2/k_F^2)^2 \tag{A10}$$

so that

$$K(T \to 0) \propto \int_0^{q_0} \frac{d^3 q}{v_F q} \int_0^{\infty} \frac{\kappa\, d\kappa}{e^{\kappa} - 1} \frac{1}{A^2} \quad , \tag{A11}$$

where we have made the change of variables $\kappa = \omega/T$. Hence

$$K \propto \int_0^{q_0} \frac{q\, dq}{(1 - \bar{I} + \bar{I}\alpha q^2/k_F^2)^2} \quad . \tag{A12}$$

Therefore the most important part of K is

$$K \propto 1/(1 - \bar{I}) \tag{A13}$$

so that

$$\delta\chi_{\text{fl}}(T) \propto J(T) \propto T^2/(1 - \bar{I}) \quad . \tag{A14}$$

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*Permanent address: Physique des Solides, Université de Paris-sud, 91405 Orsay, France.

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