Theory of NMR in heavy-fermion compounds using the slave-boson technique

S. M. M. Evans* and B. Coqblin
Laboratoire de Physique des Solides, Bâtiment 510, Université de Paris–Sud, 91405 Orsay CEDEX, France
(Received 19 October 1990)

The nuclear-spin-relaxation rate, $1/T_1$, in several of the heavy-fermion compounds has been measured. The temperature dependence of $1/T_1$ clearly reflects the T dependence of the f-electron susceptibility, χ^f, even though the experiments are performed on the non-f sites. A calculation is performed using the slave-boson approach to the periodic Anderson model. It is shown that the f-electron susceptibility does indeed give the observed T dependence of $1/T_1$ as well as that of the neutron-scattering half-width. The fact that the conduction-electron relaxation rate reflects the f-electron susceptibility can be explained by including spin fluctuations in our model. These have previously been largely ignored. We extend the calculation to the case of the noncubic Ce compounds in which anisotropy is important. We show that the anisotropy of $1/T_1$ does not reflect the magnetic anisotropy of the f electrons. The Knight shift is also considered. The enhancement of K^2 is seen to be approximately the same as for $1/(T_1T)$, but in this case the anisotropy of K is related to that of χ^f.

I. INTRODUCTION

The properties of heavy-fermion compounds have been investigated by a variety of experimental techniques.[1,2] Cerium and ytterbium compounds, in particular, have been studied by neutron-scattering experiments.[3,4] Neutron-scattering experiments provide important information concerning the anomalous magnetic properties of these compounds, indicating the presence of complex incommensurate magnetic correlations in, for example, $CeCu_6$ and $CeRu_2Si_2$.[4]

Another dynamical technique which can be used to help clarify the microscopic picture is nuclear magnetic resonance (NMR) and it is primarily this technique that we consider here. The NMR relaxation rates, $1/T_1$, and the Knight shifts, K, have been measured at the Al site in $CeAl_2$ (Ref. 5) and YbCuAl,[6,7] at the Si site in $CeRu_2Si_2$,[8] and at the Cu site in $CeCu_6$,[9] and finally at both the Cu and Si sites in superconducting and nonsuperconducting $CeCu_2Si_2$.[7,10,11] At very low temperatures, the relaxation rate $1/T_1$ varies linearly with temperature up to a temperature T^*, which is equal to 0.2 K in $CeCu_6$,[9] roughly 5 K in $CeCu_2Si_2$,[10] and 8 K in $CeRu_2Si_2$.[8] Thus, below T^*, $1/T_1$ follows the Korringa law but with the value of $1/T_1T$ showing an extremely large enhancement. For example, the value of $1/(T_1T)$ as $T\rightarrow 0$ is equal to 88 $(\sec K)^{-1}$ in $CeCu_6$,[9] roughly 5 $(\sec K)^{-1}$ in $CeCu_2Si_2$,[10] and 1 $(\sec K)^{-1}$ in $CeRu_2Si_2$,[8] which can be compared with the values 0.025 $(\sec K)^{-1}$ in $LaCu_2Si_2$ (Ref. 10) and 0.014 $(\sec K)^{-1}$ in $LaRu_2Si_2$.[8] As T is increased, $1/T_1T$ becomes temperature dependent, with $1/T_1$ reaching a plateau for $T\sim T_K$, where T_K is the Kondo temperature. At still higher temperatures, there is a slow decrease with increasing temperature. It follows that $1/(T_1T)$ decreases very rapidly with increasing temperature in all these compounds. The low-temperature increase of $1/T_1$ also occurs in $CeAl_2$, which orders antiferromagnetically at $T_N=3.9$ K. $1/T_1$ continues to increase above the transition temperature, with no anomaly at T_N.[5]

Moreover, the relaxation rate and the Knight shift of the tetragonal compound $CeRu_2Si_2$ have been found to be clearly anisotropic. Kitaoka *et al.*[8] have measured the ^{29}Si spin-lattice-relaxation rates $1/T_{1\parallel}$ and $1/T_{1\perp}$ for an applied field perpendicular and parallel, respectively, to the c axis. $1/T_{1\perp}$ is about three times larger than $1/T_{1\parallel}$. Both increase linearly with increasing temperature up to 10 K then remain approximately constant at higher temperatures. The Knight shift K shows a large anisotropy, with the ratio $K_\parallel/K_\perp$ of the Knight shifts parallel and perpendicular to the c axis equal to 30 at 4.2 K.[8] This is comparable to the anisotropy of the magnetic susceptibility $\chi_\parallel/\chi_\perp\sim 15$ at 4.2 K. $K_\parallel$ shows a maximum around 12 K followed by a rapid decrease, while $K_\perp$ is almost temperature independent. In the case of $CeCu_2Si_2$, a very small anisotropy has been observed for the relaxation rate.[10]

The temperature dependence and the enhancement of $1/T_1$ clearly reflects the f-electron susceptibility despite the fact that the experiments are performed at the non-f sites. The anisotropy, however, is much smaller than would be expected for the f electrons. In contrast, both the temperature dependence and the anisotropy of the Knight shift seem to be related to the f-electron susceptibility. The NMR experiments, therefore, yield important information not only about the f electrons but also about the relation between f- and conduction- (c)-electron sites. A model based on spin fluctuations has previously been used to account for the temperature dependence of the neutron-scattering quasielastic linewidth and the NMR relaxation rate measured at the Si site in $CeCu_2Si_2$ or at the Al site in $CeAl_2$.[12] In this model, the half-width Γ of the neutron quasielastic line is connected to the $4f$ susceptibility on the Ce atom enhanced by spin fluctuations,[13] while the relaxation rate $1/T_1$ on the noncerium

site measures the s-electron generalized susceptibility which is indirectly enhanced by the $4f$ electrons via the s-f exchange interaction.[14]

In the present paper, we consider the nuclear relaxation and the Knight shift by using the slave-boson approach to the periodic Anderson model,[15] which is appropriate to describe the low-T properties of the heavy-fermion compounds. We start by considering the energy- and k-dependent susceptibility of the f electrons $\chi^f(k,\omega)$. Relating this to $1/T_1$ in the usual way, we can calculate the T dependence of the relaxation rate for the f sites, $1/T_1^f$. It is found that this is in qualitative agreement with experiment. Assuming that the susceptibility describes a Lorentzian at low ω, we can also use $1/T_1^f$, together with $\chi^f(0,0)$, to calculate the neutron-scattering half-width. Again, this has the correct qualitative behavior. We generalize to the case where crystal-field splitting is included as is relevant for the noncubic Ce compounds. This produces an anisotropy in $1/T_1^f$. We show that the Korringa relation is approximately obeyed in each magnetic channel and in the case where one channel dominates, the anisotropy of $1/T_1^f$ is approximately equal to that of the magnetic susceptibility.

We consider next the connection between the c- and f-electron susceptibilities to produce a relation between $1/T_1$ on the c sites and $1/T_1^f$. At the mean-field level, the conduction-electron susceptibility is largely unaffected by the presence of the f electrons and the observed temperature dependence is not found. Including corrections $O(1/N)$, where N is the f-electron degeneracy, also produces no simple relation between $1/T_1$ and χ^f. In order to account for the observed properties, we need to include spin fluctuations which do not appear in the model until we go at least to order $1/N^2$. The importance of spin fluctuations in the heavy-fermion compounds has already been suggested by Doniach[16] and Houghton *et al.*[17] although, in general, they have largely been ignored. Following Doniach,[16] we perform a ladder summation to obtain a Stoner susceptibility in which the "bare" susceptibilities are those coming from the mean-field quasiparticle bands. The calculation now becomes somewhat analogous to that of Jullien and Coqblin[14] for describing NMR experiments on nearly magnetic ions in metallic hosts, and it is shown that $1/T_1$ is straightforwardly related to $1/T_1^f$. We consider again the problem of the anisotropy. By using a realistic model in which the c electrons have spin $\pm\frac{1}{2}$ as opposed to the "spin-N" model frequently used, we show that the anisotropy of $1/T_1^f$ is not reflected in the relaxation on the c-electron sites and the only anisotropy comes from the anisotropic hyperfine constants.

Finally, we calculate the Knight shift K. It is shown that K^2 has approximately the same enhancement as $1/T_1T$ and the anisotropy is directly related to the magnetic anisotropy of the f electrons. These theoretical results are successfully compared with the experimental data in the heavy-fermion compounds.

II. RELAXATION ON THE f SITES

The nuclear relaxation rate is related to the susceptibility $\chi(q,\omega)$ in the following way:

$$\frac{1}{T_1T}=2\gamma_n^2k_B\sum_q[A_{\rm hf}(q)]^2\lim_{\omega\to0}\left[\frac{{\rm Im}\chi(q,\omega)}{\omega}\right], \quad (2.1)$$

where $A_{\rm hf}(q)$ is the spatial Fourier transform of the hyperfine field from the magnetic ion at R_{ij}, $A_{\rm hf}(R_{ij})$. We neglect the q dependence of $A_{\rm hf}(q)$ and consider

$$\sum_q\lim_{\omega\to0}[{\rm Im}\chi(q,\omega)/\omega] .$$

In this section, we consider this quantity calculated for the f electrons and postpone the discussion of how this is related to NMR on the c sites until Sec. III. Within the slave-boson approach to the periodic Anderson model, the effective Hamiltonian is written[15]

$$H=\sum_{k,m}\varepsilon_kc_{km}^\dagger c_{km}+\sum_{j,m}\varepsilon_ff_m^{j\dagger}f_m^j + \sum_{k,j,m}(\tilde{V}e^{iR_j\cdot k}c_{km}^\dagger f_m^j+{\rm H.c.})+i\lambda(\rho^2-1) , \quad (2.2)$$

where $\tilde{V}=\rho V$ and $\varepsilon_f=E_0+i\lambda$. ρ and $i\lambda$ are the mean-field parameters which are determined by minimizing the free energy. This gives $\rho^2=1-n_f$, where n_f is the mean f valence. $\varepsilon_f\sim T_K$ gives the energy scale for the system. We have used the "spin-N" model where both the f and c electrons are characterized by an N-fold degenerate spin-quantum number m. The theory then develops as an expansion in $1/N$.

The magnetic susceptibility is defined as

$$\chi^{fi}(q,t)=\langle\mathcal{T}_t[S^{fi}(q,t)S^{fi}(-q,0)]\rangle , \quad (2.3)$$

where

$$S^{fi}(q)=\sum_{k,m,m'}\alpha_{mm'}^if_{km}^\dagger f_{k+q,m'} , \quad (2.4)$$

with similar expressions for the c electrons. $\alpha_{mm'}^i=\langle m|\mu_i|m'\rangle$, where i is the direction of the magnetic field and μ_i is the magnetic moment along the i axis. With use of the mean-field Hamiltonian (2.2), the f-electron susceptibility is given by

$$\chi^f(q,\omega)=\mu_0^2\sum_{k,\nu}G^f(k+q,\omega+\nu)G^f(k,\nu) , \quad (2.5)$$

where $G^f(k,\nu)$ is the f-electron Green function,

$$G^f(k,\nu)=\frac{1}{\nu-\varepsilon_f-\tilde{V}^2/(\nu-\varepsilon_k)} =\frac{A_+(k)}{\nu-E_-(k)}+\frac{A_-(k)}{\nu-E_+(k)} , \quad (2.6)$$

$E_\pm(k)$ are the quasiparticle bands given by

$$E_\pm(k)=\tfrac{1}{2}\{\varepsilon_k+\varepsilon_f\pm[(\varepsilon_k-\varepsilon_f)^2+4\tilde{V}^2]^{1/2}\}, \quad (2.7)$$

and $A_\pm(k)$ are the f electron weights in the bands

$$A_\pm(k)=\frac{1}{2}\left[1\pm\frac{\varepsilon_k-\varepsilon_f}{E_+(k)-E_-(k)}\right] . \quad (2.8)$$

$\mu_0^2=\mu_B^2\sum_m m^2$ is the magnetic moment.

We start by considering the case with $N=2$. Using

the above expression for $G^f(k,\nu)$ in (2.6), we find a number of terms which contribute to the susceptibility: intraband terms for the lower and upper bands and interband terms between the two bands. Since $1/T_1$ involves the imaginary part as $\omega\to 0$, there will be no contribution from the interband terms which describe excitation across the hybridization gap. The contribution from the lower band can be written

$$\mathrm{Im}\tilde{\chi}^f(q,\omega)=\mathrm{Im}\sum_k A_+(k)A_+(k+q)\frac{f(E_-(k))-f(E_-(k+q))}{\omega-E_-(k+q)+E_-(k)}$$
$$=\pi\sum_k A_+(k)A_+(k+q)[f(E_-(k))-f(E_-(k+q))]\delta(\omega-E_-(k+q)+E_-(k))\ , \tag{2.9}$$

where $\tilde{\chi}^f=\chi^f/\mu_0^2$. Using the free-electron approximation

$$\varepsilon_{k+q}=\varepsilon_k+q^2/2+qk\cos\theta\ ,$$

we can integrate over the angle θ between $\mathbf{k}$ and $\mathbf{q}$. Also taking the limit as $\omega\to 0$, we find

$$\lim_{\omega\to 0}\mathrm{Im}\left[\frac{\tilde{\chi}^f(q,\omega)}{\omega}\right]$$
$$=\pi\frac{\rho_0}{2}\int dE_-\left[\frac{A_+}{A_-}\right]^2 f'(E_-)\frac{\Theta(2k-q)}{kq}\ , \tag{2.10}$$

where ρ_0 is the conduction-electron density of states, assumed to be constant. We can now perform the sum over q and obtain

$$\sum_q\lim_{\omega\to 0}\left[\frac{\mathrm{Im}\tilde{\chi}^f(q,\omega)}{\omega}\right]=\pi\rho_0^2\int dE_-\left[\frac{A_+}{A_-}\right]^2 f'(E_-)\ , \tag{2.11}$$

where it can be shown that

$$A_+/A_-=\tilde{V}^2/(E_--\varepsilon_f)^2\ .$$

At $T=0$ this is easily evaluated and comparison with $\chi_f(0,0)$ shows that the Korringa relation is obeyed, i.e.,

$$\sum_q\lim_{\omega\to 0}\left[\frac{\mathrm{Im}\tilde{\chi}^f(q,\omega)}{\omega}\right]=\pi[\tilde{\chi}_f(0,0)]^2\ , \tag{2.12}$$

where $\tilde{\chi}^f(0,0)=\rho_0\tilde{V}^2/\varepsilon_f^2$.

It follows that the low-temperature value of $1/(T_1T)$, $1/(T_1T)_0$, is given by

$$\frac{1}{(T_1T)_0}=2\gamma_n^2 k_B\bar{A}_{\mathrm{hf}}^2\left[\rho_0\frac{m^*}{m}\right]^2\ . \tag{2.13}$$

Thus, the enhancement of $1/(T_1T)_0$ is given by the square of the heavy-fermion effective mass, just as the enhancement of the T^2 term in the low-temperature resistivity.

The calculation can be extended numerically to finite temperatures. Terms from the upper band also need to be included. These are given by (2.11) with $E_-\to E_+$. At high temperatures we expect $1/T_1^fT\sim 1/T$ and, as the characteristic temperature scale in the problem is T_K, we expect the crossover from $1/T_1T=$const to $1/T_1T\sim 1/T$ to take place over a temperature range $\sim T_K$. We need to also include the T dependence of the mean-field parameters ε_f and n_f. Here we encounter a problem. The mean-field solution has an artificial phase transition at a temperature T_c at which point $n_f=1$. It can be shown that as $n_f\to 1$, $1/T_1T\sim 1/\tilde{V}^2$ and so diverges. If, however, we suppress the temperature dependence of n_f by allowing for the temperature dependence of μ, the Fermi level, T_c is pushed to high temperatures and we obtain sensible results around T_K.[18]

The low-temperature behavior found using this procedure is shown in Fig. 1. The peak found at low T depends sensitively on the filling factor x, where x, the number of electrons in the band, is between 0 and 2. This nonuniversal behavior can be contrasted with the susceptibility where χ^f varies little with x. This is interesting in view of the fact that, experimentally, the temperature T^* at which $1/T_1T$ ceases to be constant varies greatly from compound to compound, e.g., $T^*=0.03T_K$ for $CeCu_6$ (Ref. 9) compared to $T^*\sim 0.7T_K$ for $CeRu_2Si_2$.[8] Experimentally there is no evidence for a low-temperature peak. We note, however, that the peak arises from a very small positive curvature in $1/T_1$, which may not be clear experimentally. At higher temperatures, $1/T_1$ saturates as shown on the curve plotted in Fig. 2 for $x=1.5$ ($J=0$).

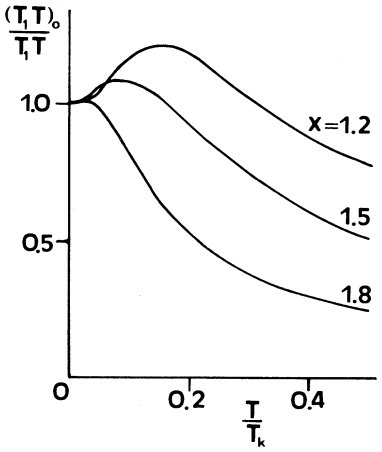

FIG. 1. $(T_1T)_0/T_1T$ against T/T_K at low temperatures for $x=1.2$, 1.5, and 1.8, where $(T_1T)_0$ is the zero-temperature limit of T_1T.

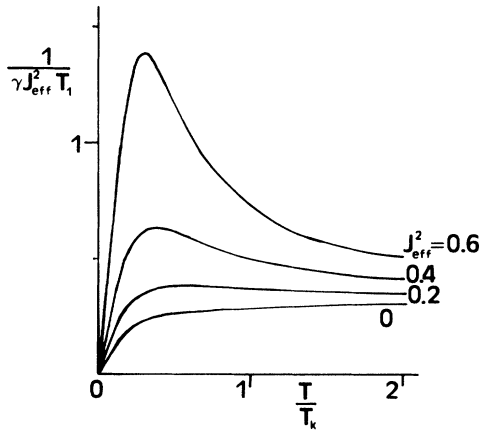

FIG. 2. $1/\gamma J_{\rm eff}^2 T_1$ against T/T_K for $J_{\rm eff}=0$, 0.2, 0.4, and 0.6 with $\gamma=2\gamma_n^2 k_B \overline{A}_{\rm hf}^2$.

While the value at which it saturates depends on x, the temperature at which it does so is roughly T_K in all cases. Thus, the present theoretical model accounts fairly well for the experimental results in heavy-fermion compounds and, in particular, for the low-temperature Korringa behavior with an enormous value of $1/(T_1T)_0$ and the saturation of $1/T_1$ above T_K.

Let us now consider the problem of the relaxation rate in noncubic cerium compounds. In this case, crystal-field effects are important as previously established for the resistivity[19] and the magnetic field susceptibility.[20] The f-level degeneracy, originally 6, is split and we have three doublets with renormalized energies ε_{0f}, $\varepsilon_{1f}=\varepsilon_{0f}+\Delta_1$, and $\varepsilon_{2f}=\varepsilon_{0f}+\Delta_2$, where Δ_1 and Δ_2 are the crystal-field splittings. Within the mean-field approximation, we get six hybridized subbands, $E_{n\pm}$, where $n=0$, 1, and 2 runs over the three doublets. The susceptibility is now given by

$$\chi^{fi}(q,\omega)=\sum_{m,m'}\chi^{fi}_{mm'}(q,\omega)$$
$$=\sum_{m,m'}|\alpha^i_{mm'}|^2\tilde{\chi}^f_{mm'}(q,\omega)\ , \tag{2.14}$$

where

$$\tilde{\chi}^f_{mm'}(q,\omega)=\sum_{k,\nu}G^f_m(k+q,\omega+\nu)G^f_{m'}(k,\nu)\ . \tag{2.15}$$

G^f_m is given by (2.6) with $E_\pm\rightarrow E_{m\pm}$. m is here defined as an eigenstate of the crystal field.

When we look at the relaxation as $T\rightarrow 0$, we find that there are both intraband and interband terms. For the intraband terms we can easily generalize from (2.12) to obtain

$$\sum_q\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\tilde{\chi}^f_{mm}(q,\omega)}{\omega}\right]=\pi[\tilde{\chi}^f_{mm}(0,0)]^2\ . \tag{2.16}$$

Since the field mixes terms with m and m', we need also to consider terms coming from $\chi^f_{mm'}$. The calculation proceeds in a similar way as before, giving

$$\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\tilde{\chi}^f_{mm'}(q,\omega)}{\omega}\right]=\pi\rho_0\int dE_{m-}\frac{\tilde{V}^2}{(E_{m-}-\varepsilon_{mf})^2}\frac{\tilde{V}^2}{(E_{m'-}-\varepsilon_{m'f})^2}f'(E_{m-})$$
$$\times\frac{\Theta(E_{m-}(k)-E_{m'-}(k+q,-1))\Theta(E_{m'-}(k+q,+1)-E_{m-}(k))}{kq}\ , \tag{2.17}$$

where $E_{m-}(k+q,\pm 1)=E_{m-}(k+q,\cos\theta=\pm 1)$. In general, it is difficult to perform the sum over q due to the Θ functions. At $T=0$, however, the expression simplifies and we find

$$\sum_q\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\chi^f_{mm'}(q,\omega)}{\omega}\right]=\pi a\left[\rho_0\frac{\tilde{V}^2}{\varepsilon_{mf}\varepsilon_{m'f}}\right]^2\ , \tag{2.18}$$

where a is a constant between 0.5 and 1 which depends on the crystal-field splitting. Calculating the analogous terms in $\chi^f_{mm'}(0,0)$, we find

$$\chi^f_{mm'}(0,0)\sim\frac{\rho_0\tilde{V}^2}{(\varepsilon_{mf}\varepsilon_{m'f})}\ ,$$

where the corrections are of order $(\ln\Delta)/\Delta$ for large crystal-field splitting. Then, approximately,[20]

$$\sum_q\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\tilde{\chi}^f_{mm'}(q,\omega)}{\omega}\right]=\pi[\tilde{\chi}^f_{mm'}(0,0)]^2\ . \tag{2.19}$$

To a reasonable accuracy, therefore, we obtain the result that the Korringa relation works for each term in the summation over m and m'.

We can then relate ${\rm Im}\chi^f$ parallel and perpendicular to the c axis to $1/T_1^fT$ measured parallel and perpendicular to the c axis in the following way:[8]

$$\left[\frac{1}{T_1^fT}\right]_\parallel=2\gamma_n^2k_B\sum_q 2A^2_{{\rm hf}\perp}\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\chi^f_\perp(q,\omega)}{\omega}\right]\ , \tag{2.20}$$

$$\left[\frac{1}{T_1^fT}\right]_\perp=2\gamma_n^2k_B\sum_q\left[A^2_{{\rm hf}\parallel}\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\chi^f_\parallel(q,\omega)}{\omega}\right]+A^2_{{\rm hf}\perp}\lim_{\omega\rightarrow 0}\left[\frac{{\rm Im}\chi^f_\perp(q,\omega)}{\omega}\right]\right]\ , \tag{2.21}$$

where $\chi_\perp=\chi^x=\chi^y$ and $\chi_\parallel=\chi^z$. In general, there is no simple relation between the total susceptibility and the

relaxation. In many cases, however, the low-T susceptibility is dominated by a single term and, in this case, the Korringa relation will work. Calculating, for example, the anisotropy of $1/T_1T$ using the experimentally deduced parameters for the crystal-field levels in $CeRu_2Si_2$,[21] we find

$$\frac{\sum_q \lim_{\omega\to 0}\left[\mathrm{Im}\chi_{\parallel}^f/\omega\right]}{\left[\sum_q \lim_{\omega\to 0}(\mathrm{Im}\chi_{\perp}^f/\omega)\right]}\approx 13 ,$$

and, so if we take the A_{hf}'s as being equal, we find

$$\frac{(T_1T)_{\perp}^{-1}}{(T_1T)_{\parallel}^{-1}}\approx 7 ,$$

compared with $\chi_{\parallel}(0)/\chi_{\perp}(0)\approx 11$.[20] The calculation can also be extended to finite temperatures. With the same parameters we find that the shape of both $1/T_{1\parallel}$ and $1/T_{1\perp}$ is roughly the same as that found in Fig. 1 for $J_{\mathrm{eff}}=0$. Up to T of the order of $1.5T_K$ the anisotropy varies very little from its value at $T=0$ and above this temperature the anisotropy decreases rapidly as shown in Fig. 3, where we have plotted both $T_{1\parallel}^f/T_{1\perp}^f$ and $\chi_{\parallel}^f/\chi_{\perp}^f$ as a function of T/T_K. The crystal-field levels lie at approximately $10T_K$ and $50T_K$ above the ground-state doublet. We see in Fig. 3 that the ratio $T_{1\parallel}^f/T_{1\perp}^f$ is still larger than 1 for $T=25T_K$. This corresponds to $T=0.5\Delta_2$, and so we are not yet in the region $T\gg\Delta_2$, where we expect the anisotropy to disappear. The disappearance of the anisotropy at very high temperatures has been checked by the classical perturbation-theory calculation at temperatures high compared with T_K within the simple method previously used to derive the resistivity.[19] We have calculated the relaxation rate of the doublet ground state in a noncubic cerium Kondo alloy or compound within the perturbation theory up to third order in the exchange integrals of the Coqblin-Schrieffer Hamiltonian with crystal-field effects as previously done for AuYb (Ref. 22) alloys and we have shown that there is no anisotropy in the relaxation rate in contrast to the case of the resistivity.[19]

Thus, the consideration of the relaxation rate directly measured on the f site can yield a very large theoretical anisotropy at low temperatures, which disagrees with the experimental data in $CeRu_2Si_2$. In Sec. III we will obtain much better agreement with experiment by considering that the relaxation rate is really measured at the Si site and not directly at the Ce site in these compounds.

It is also interesting to consider the neutron-scattering half-width Γ_q. Experimentally it is found that the data are reasonably well fitted with a Lorentzian for the imaginary part of the susceptibility.[23] We assume that

$$\mathrm{Im}\left[\frac{\tilde{\chi}^f(q,\omega)}{\omega}\right]=\tilde{\chi}(q,0)\frac{\Gamma_q}{\Gamma_q^2+\omega^2} . \tag{2.22}$$

This form is also found approximately from the slave-boson technique for small Fermi surfaces.[24] It is then easily shown that

$$\Gamma_q=\frac{\tilde{\chi}^f(q,0)}{\lim_{\omega\to 0}[\mathrm{Im}\tilde{\chi}^f(q,\omega)/\omega]} . \tag{2.23}$$

For small q and ω we can approximate $\chi(q,0)=\chi(0,0)$; then, using (2.11), we find, at $T=0$,

$$\Gamma_0=\frac{2Nq}{\pi k_F}T_K . \tag{2.24}$$

This is just the result found by Lopes *et al.*[13] for the small-q limit, with $N=2$, in a spin-fluctuation model, with T_K replaced by T_{SF}, the spin-fluctuation temperature. The temperature dependence of Γ_q has been calculated and a typical curve is shown in Fig. 4: the half-width starts from the finite value given by (2.24) and after a small initial decrease it increases slowly with a negative curvature and almost saturates at higher temperatures. The curve shown in Fig. 4 has the typical shape of the neutron quasielastic linewidth observed experimentally in

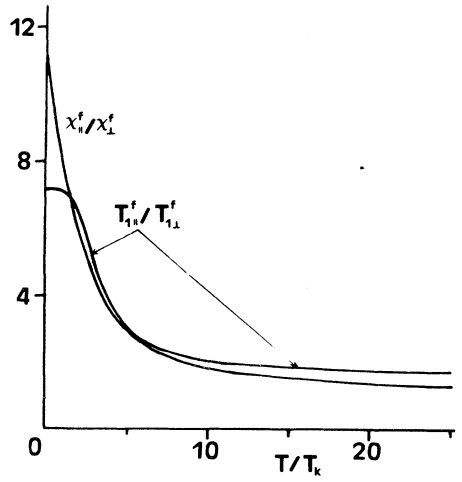

FIG. 3. $T_{1\parallel}^f/T_{1\perp}^f$ and $\chi_{\parallel}^f/\chi_{\perp}^f$ against T/T_K. Parameters are as for $CeRu_2Si_2$.

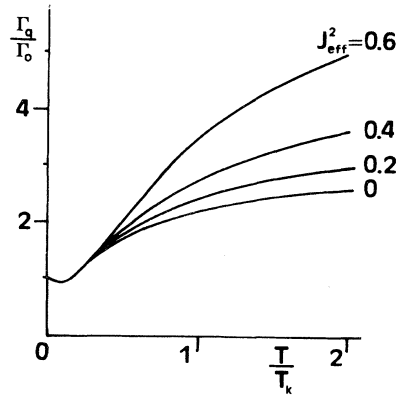

FIG. 4. Γ_q/Γ_0 against T/T_K for $J_{\mathrm{eff}}=0$, 0.2, 0.4, and 0.6, where Γ_0 is the zero T value of Γ.

many cerium compounds[3,4,13] and, for example, in $CeCu_6$ (Ref. 4) and $CeRu_2Si_2$.[25] In particular, it is experimentally observed that the very low-temperature value of the half-width has a finite value proportional to T_K and the half-width increases slowly with increasing temperature as theoretically derived here. We will go back to this problem in Sec. III where a better agreement with experiment will be obtained at high temperatures.

III. SPIN FLUCTUATIONS

The temperature dependence of the f-electron susceptibility appears to account reasonably well for the observed relaxation rate but not for the observed anisotropy and we will now try to improve the preceding model. We need to consider how the NMR on the c sites is related to χ^f. We note that, if we simply use the mean-field susceptibility for c, χ^c, we neither get the correct temperature dependence nor the enhancement for $T\rightarrow 0$. We need to include the fluctuations in the boson propagators. To order $1/N$ this does not produce a simple relation between χ^c and χ^f and we need to go at least to order $1/N^2$ where spin fluctuations begin to play a role. In the mean-field approximation we have replaced the amplitude and phase of the boson propagator, $\rho(k,\omega)$ and $\lambda(k,\omega)$, respectively, by their average values. Following Doniach[16] we neglect the fluctuations of the phase and consider only the interaction

$$H_1=\sum_{k,k'} V\delta\rho(k-k')c^{\dagger}_{km}f_{km'}+\text{H.c.}$$

We also approximate the boson propagator

$$\langle \delta\rho(k,\omega)\delta\rho(-k,\omega)\rangle$$

by its high-frequency value $1/i\lambda\approx 1/E_0$, where E_0 is the bare f-electron energy. The other boson propagators are zero in the same limit.[17] In the Kondo limit, we can evaluate the ladder diagrams shown in Fig. 5, looking again at the case where $N=2$. The c-electron susceptibility including spin fluctuations, $\chi^c_{\rm SF}$, becomes

$$\tilde{\chi}^c_{\rm SF}(q,\omega)=\frac{\tilde{\chi}^c(q,\omega)}{1-J^2\tilde{\chi}^c(q,\omega)\tilde{\chi}^f(q,\omega)}, \tag{3.1}$$

where $J=V^2/E_0$. Taking the imaginary part of the susceptibility and neglecting the q dependence of

$$\mathrm{Re}[\tilde{\chi}^c(q,0)\tilde{\chi}^f(q,0)]\ ,$$

we obtain

$$\sum_q \lim_{\omega\rightarrow 0}\mathrm{Im}\left[\frac{\tilde{\chi}^c_{\rm SF}(q,\omega)}{\omega}\right]=\frac{J^2\tilde{\chi}^c\sum_q \lim_{\omega\rightarrow 0}(\mathrm{Im}\tilde{\chi}^f/\omega)}{[1-J^2\tilde{\chi}^c(0,0)\tilde{\chi}^f(0,0)]^2}\ . \tag{3.2}$$

We have neglected $\mathrm{Im}\tilde{\chi}^c$ compared with $J^2\tilde{\chi}^c\mathrm{Im}\tilde{\chi}^f$ which implies $(J\rho_0 m^*/m)^2\gg 1$. We note that if the system has ferromagnetic fluctuations, i.e.,

$$\tilde{\chi}^c(0,0)\tilde{\chi}^f(0,0)>\tilde{\chi}^c(2k_F,0)\tilde{\chi}^f(2k_F,0)\ ,$$

then, in neglecting the q dependence of the denominator, we are overestimating $1/T_1T$, while in the opposite case of antiferromagnetic fluctuations

$$\tilde{\chi}^c(0,0)\tilde{\chi}^f(0,0)<\tilde{\chi}^c(2k_F,0)\tilde{\chi}^f(2k_F,0)\ ,$$

we underestimate $1/T_1T$.

We find that $1/T_1T$ as measured on the c sites is indeed related to the susceptibility of the f sites. If we look at the order of magnitude of the experimental value of $1/T_1T$ for $CeRu_2Si_2$ compared with that for $LaRu_2Si_2$, we find that the former is enhanced by a factor $\sim 50-100$, which can be compared with a mass enhancement also $\sim 50-100$. The enhancement is not then nearly as large as it would be if NMR were performed at the f sites. If we have $J^2\rho_0^2 m^*/m\sim 1$, then the above model correctly accounts for the observed enhancement. Using the results calculated at finite temperature, we can plot $1/(J^2_{\rm eff}T_1)$ for different values of $J_{\rm eff}=J^2\rho_0^2 m^*/m$, where it is convenient to treat $J_{\rm eff}$ as an independent parameter. The results are shown in Fig. 2. From (3.2), the case $J_{\rm eff}=0$ corresponds to the case studied in Sec. II. For small $J_{\rm eff}$, we find a broad maximum at about T_K, which corresponds approximately to the experimental situation. As $J_{\rm eff}$ increases, the maximum becomes more pronounced and moves to lower T.

We again consider the problem of the magnetic anisotropy arising from the crystal-field effects. In this case, we can no longer use the "spin-N" approach used above where it is assumed that the conduction electrons have the same spin as the f electrons. This approach would imply that the factors $\alpha^i_{mm'}$ occurring in the expression for the f-electron susceptibility (2.14), also occur in that for the c-electron susceptibility. This would produce a large anisotropy in χ^c which is not realistic. It is important then to consider the real case where the c electrons have spin $\pm\frac{1}{2}$. Following Zou and Anderson,[26] the hybridization term is given by

$$\sum_{\mathbf{k},\sigma,j,m}[V_{m\sigma}(\mathbf{k})e^{iR_j\cdot\mathbf{k}}c^{\dagger}_{\mathbf{k}\sigma}f^j_m+\text{H.c.}]\ . \tag{3.3}$$

The hybridization matrix element is of the form

$$V_{m\sigma}(\mathbf{k})=V_0 Y_{3m-\sigma}(\mathbf{k})\langle 3lm-\sigma,\tfrac{1}{2}\sigma|\tfrac{5}{2}m\rangle\ ,$$

where $Y_{3m-\sigma}(\mathbf{k})$ is the spherical harmonic for $l=3$ and

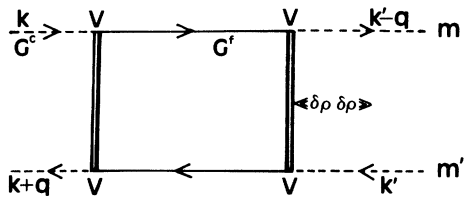

FIG. 5. The ladder diagram contributing to $\tilde{\chi}^c_{mm'}(q,\omega)$.

$$\langle 3lm-\sigma,\tfrac{1}{2}\sigma|\tfrac{5}{2}m\rangle=(4\pi)^{1/2}\left[\frac{7-4\sigma m}{14}\right]^{1/2}$$

is the Clebsch-Gordan coefficient for spin-orbit-coupled states with $j=\frac{5}{2}$ and $l=3$.

For simplicity we consider the case where the crystal-field levels are eigenstates of μ_z. It is convenient to define linear combinations of f_m and f_{-m} which hybridize with the conduction electrons of a given spin,[20]

$$f_{n\sigma}=\frac{1}{(|V_{m\sigma}|^2+|V_{-m\sigma}|^2)^{1/2}}(V_{m\sigma}f_m+V_{-m\sigma}f_{-m}), \tag{3.4}$$

where $n=0$, 1, and 2 runs over the three f-electron doublets. The expression for χ^c now involves

$$S^{ci}(q)=\sum_{k,\sigma,\sigma'}\alpha^i_{\sigma\sigma'}c^\dagger_\sigma(k)c_{\sigma'}(k+q)\ , \tag{3.5}$$

where $\alpha^i_{\sigma\sigma'}=\langle\sigma|\mu^i|\sigma'\rangle$. The ladder summation becomes more complicated as the interaction now depends on k and the terms cannot, in general, be factorized to give the Stoner susceptibility. If, however, we assume the c-electron Green function does not depend sensitively on the direction of k, we can average over direction and sum the diagrams shown in Fig. 6 and obtain

$$\chi^{ci}_{\rm SF}=\sum_{\sigma\sigma'}|\alpha^i_{\sigma\sigma'}|^2\frac{\tilde\chi^c_{\sigma\sigma'}}{1-J^2\tilde\chi^c_{\sigma\sigma'}\sum_{nn'}\tilde\chi^f_{n\sigma n'\sigma'}}\ , \tag{3.6}$$

where $\tilde\chi^f_{n\sigma n'\sigma'}$ is defined in terms of $G^f_{n\sigma}$, the Fourier transform of $\langle\langle f_{n\sigma};f^\dagger_{n\sigma}\rangle\rangle$. It is easily seen that $G^c_\sigma=G^c_{-\sigma}$ and $G^f_{n\sigma}=G^f_{n-\sigma}$ and it is therefore clear that the only place where the direction of h plays a role is in the terms $\alpha_{\sigma\sigma'}$ which, for the spin $\frac{1}{2}$ considered here, are isotropic. We note that this is independent of the approximation in which we have averaged over direction for the hybridization matrix elements. It appears then that the relaxation rate does not reflect the magnetic anisotropy of the f electrons. The only anisotropy comes from the anisotropy of the hyperfine constants. To obtain $A_{\rm hf}$ we need to know the relation between the Knight shift and the susceptibility which we consider in the next section.

Finally, we compute the half-width Γ_q of the neutron-scattering quasielastic line using (2.22), but with χ^f replaced by $\chi^f_{\rm SF}$, where

$$\tilde\chi^f_{\rm SF}(q,\omega)=\frac{\tilde\chi^f(q,\omega)}{1-J^2\tilde\chi^c(q,\omega)\tilde\chi^f(q,\omega)}\ . \tag{3.7}$$

The results are shown in Fig. 4 for different values of $J_{\rm eff}$. For low temperatures, the behavior is approximately independent of $J_{\rm eff}$, but as the temperature increases, Γ_q increases more rapidly for the larger values of $J_{\rm eff}$. This smaller tendency to saturation appears to be in better agreement with experimental data given by neutron scattering in cerium Kondo compounds.

In conclusion, the consideration of the relaxation at the non-f sites does not greatly modify the temperature dependence of the relaxation rate and the quasielastic linewidth, but it drastically changes the anisotropy of the relaxation rate which disappears completely in the present model. This appears to be in qualitative agreement with experiment, since the observed anisotropy of $1/T_1$ in $CeRu_2Si_2$ is much smaller than that observed in the magnetic susceptibility.

IV. THE KNIGHT SHIFT

When we then apply an external magnetic field, the spin susceptibility of the conduction electrons produces a small magnetic field at the nucleus which adds to the applied field. It is this that gives rise to the "Knight shift." The Knight shift can be calculated as

$$K=A_{\rm hf}\sum_k\langle|u_k(0)|^2\rangle\chi_k\ , \tag{4.1}$$

where $u_k(0)$ is the conduction-electron wave function evaluated at the nucleus and $\chi_k=m_k/h$, where m_k is the magnetic moment for a particular k state. Since χ_k is strongly peaked at the Fermi level, we can, in general, factorize this expression to obtain

$$K=A_{\rm hf}\langle|u_k(0)|^2\rangle_{\rm FS}\sum_k\chi_k=A_{\rm hf}\langle|u_k(0)|^2\rangle_{\rm FS}\chi\ , \tag{4.2}$$

where the conduction-electron wave function is now averaged over the Fermi surface (FS). It has been argued[15] that, for the heavy-fermion compounds, K will not be enhanced since $\chi\sim m^*/m$, but the c-electron weight at the Fermi surface is $\sim m/m^*$ giving $K\sim 1$. The in-

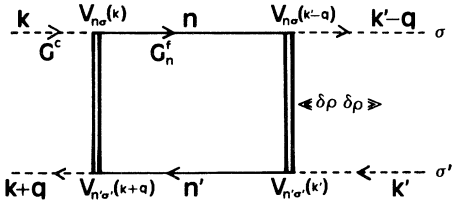

FIG. 6. The ladder diagram contributing to $\tilde\chi^c_{\sigma\sigma'}(q,\omega)$.

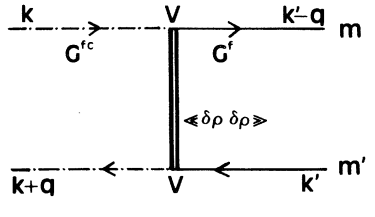

FIG. 7. The ladder diagram contributing to $\tilde\chi^f_{mm'}(q,\omega)$ to order J.

clusion of spin fluctuations would appear not to alter this argument as we may expect simply to replace χ^f by $\chi^f_{\rm SF}$ in (4.2). In fact, we shall show that this is false and by including spin fluctuations we find the expected enhancement. The error arises from the fact that we have two quasiparticle bands and the c-electron weight is not the same in the two bands. To first order in J we have terms arising from the diagrams shown in Fig. 7. This gives us

$$J|\alpha^i_{mm'}|^2\sum_k\langle|u_k|^2\rangle G^{fc}_m(k)G^{fc}_{m'}(k+q)\sum_{k'}G^f_m(k')G^f_{m'}(k'+q)=J\left[\sum_k\langle|u_k(0)|^2\rangle_{\rm FS}\tilde{\chi}^{fc}_{mm'k}(q)\right]\chi^f_{mm'}(q)\ , \tag{4.3}$$

where G^{fc}_m is the Fourier transform of $\langle\langle f_{km};c^\dagger_{km}\rangle\rangle$. The intraband contribution to $\tilde{\chi}^{fc}$ is $\sim\rho_0$ leading to a contribution to K which is ~ 1. However, there is an interband contribution to χ^{fc}, which is also $\sim\rho_0$. The c-electron weight in the upper band is ~ 1 and we obtain a term $J\rho_0\chi^f$. These terms are then renormalized by higher-order spin fluctuations to give

$$K=A_{\rm hf}\frac{J\chi^f}{1-J^2\tilde{\chi}^c\tilde{\chi}^f}\ . \tag{4.4}$$

The Korringa law is approximately the same even when the NMR experiments are performed at the c sites and K^2 has the same enhancement as $1/T_1T$. We can generalize to the case where we have anisotropy and see that, unlike the relaxation rate, K does reflect the anisotropy of the f-electron susceptibility even when NMR experiments are performed on the c sites. Thus, we can obtain a large anisotropy for K, as for the magnetic susceptibility. Since the Knight shift is proportional to the hyperfine coupling constant $A_{\rm hf}$, the difference between the observed anisotropies[8] $K_\parallel/K_\perp=30$ and $\chi_\parallel/\chi_\perp=15$ for the Knight shift and the magnetic susceptibility of $CeRu_2Si_2$ can be accounted for by taking a value of 2 for the anisotropy of $A_{\rm hf}$ which, in turn, gives an anisotropy of ~ 2.5 for $1/(T_1T)$, in good agreement with experiment.

Our calculation relates $1/(T_1T)$ and K to χ^f and the hyperfine constant $A_{\rm hf}$. Thus, we now have a way of computing the theoretical value of $1/(T_1T)$ for $CeRu_2Si_2$, without involving $A_{\rm hf}$. We find

$$\left[\frac{1}{T_1T}\right]_\perp=2\gamma_n^2k_BC_c\left[\frac{K_\parallel}{C_{f\parallel}}\right]^2, \tag{4.5}$$

where $C_{f\parallel}$ and C_c are the Curie constants for the f electrons, as measured parallel to the c axis, and the conduction electrons, respectively. Taking the value $C_{f\parallel}=(1.29\mu_B)^2$ used by Kitaoka *et al.*,[9] $C_c=\mu_B^2$ and the experimental value of $K_\parallel$ gives us a calculated value of $1/(T_1T)_\perp=1.5\ (\sec K)^{-1}$, compared with the experimental value of 1 $(\sec K)^{-1}$. We note that our calculated value is smaller than that calculated by Kitaoka *et al.*[8] They used the f-electron susceptibility directly and the results differ by a factor $C_{f\parallel}/C_c$.

V. CONCLUSION

We have seen that the calculated temperature dependence of the f-electron magnetic susceptibility can account qualitatively for the observed temperature dependence of the relaxation rate in NMR experiments. In order for the f-electron susceptibility to control $1/T_1$ measured on the non-f sites, it is important to include spin fluctuations in our theory. In this case, $1/T_1$ is indeed directly related to χ^f with a new feature, namely a broad maximum in $1/T_1$, also appearing. The model can also account for the very large enhancement observed in $1/T_1T$ as $T\to 0$. The Knight shift is also shown to be enhanced in agreement with experiment where it is seen that the Korringa relation is approximately correct implying K^2 must have the same enhancement as $1/T_1T$. It is seen that $1/T_1T$ measured along and perpendicular to the c axis does not reflect the magnetic anisotropy of the f sites. In contrast, the anisotropy of K is proportional to that of χ. By comparing the anisotropy of K with that of χ, we can therefore deduce the anisotropy of the hyperfine constant and hence calculate the anisotropy of $1/(T_1T)$. This procedure has been applied to $CeRu_2Si_2$ giving good agreement with experiment. There is, therefore no need to account for a further anisotropy in $1/(T_1T)$ coming from the f-electron susceptibility. Finally, we note that the calculated value of $1/T_1T$ is a factor 1.5 bigger than that measured experimentally. It is possible that this reflects the presence of ferromagnetic correlations. Experimentally, neutron scattering indicates the presence of incommensurate magnetic correlations in zero magnetic field which are destroyed as a field is turned on. Since NMR experiments are performed in an applied field, it is possible that this is the correct interpretation of our result. In fact, there appear to be other shortcomings of the calculation (for example, using the free-electron approximation) and it is difficult to draw conclusions from such a small factor. The fact that our model appears to account so well for the observed experimental results appears to be direct evidence for the importance of spin fluctuations in these systems.

ACKNOWLEDGMENTS

One of us (S.M.M.E.) would like to thank the Royal Society (London) for financial support.

*Present address: Department of Mathematics, Imperial College, 180 Queens Gate, London SW17 8UE, U.K.

[1]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[2]For an extensive review see *Proceedings of the 6th International Conference on Crystal Field Effects and Heavy Fermion Physics,* Frankfurt, Germany, 1988 [J. Magn. Magn. Mater. **76&77** (1988)].

[3]S. Horn, F. Steglich, M. Loewenhaupt, and E. Holland-Moritz, Physica B **107**, 103 (1981).

[4]J. Rossat-Mignod, L. P. Regnault, J. L. Jacoud, C. Vettier, P. Lejay, J. Flouquet, E. Walker, D. Jaccard, and A. Amato, J. Magn. Magn. Mater. **76&77**, 376 (1988).

[5]D. E. Mac Laughlin, O. Pena, and M. Lysak, Phys. Rev. B **23**, 1039 (1981).

[6]D. E. Mac Laughlin, F. R. de Boer, J. Bijvoet, P. F. de Chatel, and W. C. M. Mattens, J. Appl. Phys. **50**, 2094 (1979).

[7]D. E. Mac Laughlin, J. Magn. Magn. Mater. **47&48**, 121 (1985).

[8]Y. Kitaoka, H. Arimoto, Y. Kohori, and K. Asayama, J. Phys. Soc. Jpn. **54**, 3236 (1985).

[9]Y. Kitaoka, K. Fujiwara, Y. Kohori, K. Asayama, Y. Ōnuki, and T. Komatsubara, J. Phys. Soc. Jpn. **54**, 3686 (1985).

[10]J. Aarts, F. R. de Boer, and D. E. Mac Laughlin, Physica B **121**, 162 (1983).

[11]Y. Kitaoka, K. Ueda, T. Kohara, K. Asayama, Y. Ōnuki, and T. Komatsubara, J. Magn. Magn. Mater. **52**, 341 (1985).

[12]Nguyen Ngoc Thuan, L. C. Lopes, and B. Coqblin, Phys. Rev. B **33**, 4522 (1986).

[13]L. C. Lopes, Y. Lassailly, R. Jullien, and B. Coqblin, J. Magn. Magn. Mater. **31-34**, 251 (1983).

[14]R. Jullien and B. Coqblin, J. Phys. (Paris) Lett. **35**, L197 (1974).

[15]A. J. Millis and P. Lee, Phys. Rev. B **35**, 3394 (1987).

[16]S. Doniach, Phys. Rev. B **35**, 1814 (1987).

[17]A. Houghton, N. Read, and H. Won, Phys. Rev. B **37**, 3782 (1988).

[18]S. M. M. Evans, T. Chung, and G. A. Gehring, J. Phys.: Condens. Matter **1**, 10473 (1989).

[19]A. K. Bhattacharjee, B. Coqblin, M. Raki, L. Forro, C. Ayache, and D. Schmitt, J. Phys. (Paris) **50**, 2781 (1989).

[20]S. M. M. Evans, J. Phys.: Condens. Matter **2**, 9097 (1990).

[21]A. Lacerda, A. de Visser, P. Haen, P. Lejay, and J. Flouquet, Phys. Rev. B **40**, 8759 (1989).

[22]F. Gonzalez-Jimenez, B. Cornut, and B. Coqblin, Phys. Rev. B **11**, 4674 (1975).

[23]G. Aeppli, A. Goldman, G. Shirane, E. Bucher, and M.-Ch. Lux-Steiner, Phys. Rev. Lett. **58**, 808 (1987).

[24]A. Auerbach, Ju. H. Kim, K. Levin, and M. R. Norman, Phys. Rev. Lett. **60**, 623 (1988).

[25]L P. Regnault, W. A. C. Erkelens, J. Rossat-Mignot, P. Lejay, and J. Flouquet, Phys. Rev. B **38**, 4481 (1988).

[26]Z. Zou and P. W. Anderson, Phys. Rev. Lett. **57**, 2073 (1986).