PHYSICAL REVIEW B VOLUME 49, NUMBER 18 1 MAY 1994-II

Analysis of spectroscopic data in Kondo systems

Tabish Qureshi and Sushanta Dattagupta
School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India

(Received 30 September 1993; revised manuscript received 28 December 1993)

The dynamics of the impurity spin in the Kondo problem has been studied in detail in the context of specific spectroscopic tools. The bosonized form of the Kondo Hamiltonian has been used to derive complete line-shape expressions relevant for interpreting NMR, Mössbauer, and ESR experiments. The calculation is equivalent to the so-called dilute-bounce-gas approximation in the treatment of the recently introduced spin-boson Hamiltonian. Analytical results are derived for longitudinal and transverse relaxation rates, NMR Knight shift, and the ESR g shift. From these, several known perturbative results, including the Abrikosov law, are recovered as special cases. The more general results derived here have been used to analyze a wide variety of spectroscopic data and the fits are found to be very satisfactory.

I. INTRODUCTION

Recently there has been a resurgence of interest in the classic problem of a localized magnetic moment in a metallic environment, in view of the applicability of its variants to electron *assisted* tunneling in glasses,[1] behavior of certain uranium-based heavy fermion materials,[2] and resistivity in heavily doped conducting polymers,[3] among others. Models such as the multichannel-spin-$\frac{1}{2}$ Kondo system and the two-impurity Kondo system are topics of current research.[4] Their behavior is very different from the single-impurity one-channel, conventional Kondo system. Understanding of the conventional Kondo system itself has increased tremendously after the exact diagonalization of the Hamiltonian.[5] However, the dynamics of the impurity spin cannot be calculated exactly and various perturbation techniques have been employed with varying degrees of success. The dynamic aspects of the impurity spin, in the context of specific experimental probes, is the issue we wish to address in the present investigation.

While studying dynamic properties, one is mainly interested in the relaxational behavior of the impurity spin. The latter can be investigated through a variety of experimental probes such as the impurity NMR, host near-neighbor NMR, the Mössbauer, the electron-spin-resonance (ESR), and the magnetic neutron-scattering spectroscopies. The system studied is a dilute magnetic impurity in a nonmagnetic metallic host. We briefly describe different theoretical approaches employed to interpret various spectroscopic data. All approaches use the conventional Kondo Hamiltonian[6]

$$\mathcal{H}_K = J\mathbf{S}\cdot\mathbf{s}(0) + \sum_{\mathbf{k},\sigma} \varepsilon(\mathbf{k}) c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} , \tag{1}$$

where operators $c^\dagger_{\mathbf{k}\sigma}$ create electrons of wave vector $\mathbf{k}$, energy $\varepsilon(\mathbf{k})$, and spin index $\sigma=\pm1$. The spin $\mathbf{S}$ represents the impurity spin localized at $\mathbf{r}=0$, which is assumed to be one half and $\mathbf{s}(0)$ is the effective spin of all the conduction electrons at $\mathbf{r}=0$. The parameter J is the strength of the exchange interaction between the localized spin and the conduction electrons and is positive for antiferromagnetic interaction, as is the usual situation in real metals. The quantity ρJ is a dimensionless variable of the problem where ρ represents the density of states at the Fermi energy. One other parameter which enters all calculations is a high-energy cutoff D for the excitations.

In very early attempts H_K was treated perturbatively up to second order in ρJ to yield for the relaxation rate[7]

$$\gamma = \frac{\pi k_B}{\hbar}(\rho J)^2 T , \tag{2}$$

which has the "Korringa form." The first "Kondo correction" appears in the third-order perturbation term

$$\gamma = \frac{\pi k_B}{\hbar}(\rho J)^2 T[1-2\rho J \ln(k_B T/D)] . \tag{3}$$

The next correction has a term such as $(\rho J)^4 \ln^2(k_B T)$ and so on. One can easily see that for the series to be convergent it is not ρJ but the product $\rho J\cdot\ln(k_B T/D)$ that has to be a small parameter but this is not the case near the so-called Kondo temperature

$$T_K = (D/k_B)\exp(-1/\rho J) . \tag{4}$$

Using a diagrammatic method Abrikosov had shown that summing the most divergent terms to all orders in ρJ leads to an expression for the relaxation rate which depends only on one parameter T_K (Ref. 8)

$$\gamma = \frac{\pi k_B}{\hbar} T[\ln(T/T_K)]^{-2} . \tag{5}$$

This expression is very satisfactory for $T \gg T_K$ but again diverges at temperatures close to T_K. In an attempt to remove the so-called Kondo divergences, Götze and Schlottmann considered the exchange coupling to be anisotropic with two components $J_\parallel$ and $J_\perp$.[9] Using the ideas of Anderson and Yuval[10] they treated $J_\perp$ perturbatively and obtained consistent results by numerically solving certain nonlinear equations. These results were used to interpret the experimentally obtained Cu:Fe relaxation rates and the hyperfine field at the probe nucleus.

On the experimental scene, different groups had employed different theoretical pictures to explain the mea-

0163-1829/94/49(18)/12848(12)/$06.00 ©1994 The American Physical Society

sured relaxation rates depending on the technique being used and the system under study. For Mössbauer spectroscopy experiments third-order relaxation theory was employed which yielded the relaxation rate (3).[11] In relatively recent studies at very low temperatures the Abrikosov law given by (5) showed a better agreement.[12] Mössbauer spectroscopy has also been used to measure the hyperfine field acting on the impurity nucleus[13] and the analysis was done using a Curie-Weiss form of the local polarizing field that has a temperature dependence $1/(T+T_K)$. ESR experiments were also analyzed using the Abriksov law[14] and later with an improved calculation taking into account the effect of the applied magnetic field.[15] This theoretical analysis was not very satisfactory because the value of T_K came out to be surprisingly low and the values of T_K obtained from the relaxation rate and the g shift differed by four orders of magnitude. Satellite NMR experiments have been used to extract the impurity spin-relaxation rate and the hyperfine field acting on the probe nucleus.[16,17] While the relaxation rates for Cu:Fe were explained using the calculations of Götze and Schlottmann,[9] the Knight shift was analyzed using the Curie-Weiss law, and also using Wilson's numerical renormalization-group calculation for the spin susceptibility.[18]

In the light of the preceding discussion, we feel that there is a need for a comprehensive and unified theoretical framework for deriving analytical results which take care of the Kondo divergence and can be applied to any experiment at all temperatures of practical interest. The effect of the external magnetic field on the relaxation rates which is of importance at low temperatures[14] should also be built in. Thus the purpose of this paper is to obtain complete line-shape expressions relevant for the NMR, ESR, and Mössbauer experiments starting from a fully quantum-mechanical and microscopic model. The idea is to treat the exchange constant J to all orders and still be able to calculate a general expression for the line shape. From the latter should emerge quantities such as the relaxation rate γ, whose temperature dependence is valid at all temperatures of practical interest as opposed to results such as (5), which may be good otherwise but are invalid at temperatures close to T_K.

II. THEORETICAL MODEL

A. Hyperfine interaction in a Kondo impurity

The object of the present investigation is to study the effect of the conduction electrons on the *nuclear* spin I of the impurity through the hyperfine interaction. For simplicity we restrict the present discussion to a case where the hyperfine interaction is *uniaxial.* We assume that the external magnetic field in magnetic-resonance experiments acts along the z axis. Thus the Hamiltonian that describes the uniaxial hyperfine interaction of the nuclear spin I with the electronic spin $\mathbf{S}$ of the Kondo impurity, in contact with a conduction electron bath, can be written as

$$\mathcal{H}= AI_zS_z+\hbar\omega_N I_z+\hbar\omega_e S_z-J\mathbf{S}\cdot\mathbf{s}(0)+\sum_{\mathbf{k},\sigma}\varepsilon(\mathbf{k})c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}\ , \tag{6}$$

where A is the hyperfine coupling parameter and ω_N and ω_e are the Larmor frequencies of the nuclear and the electronic spin, respectively, in the external field. The spin I may either be the nuclear spin of the impurity atom in conventional NMR (Ref. 19) and Mössbauer studies,[12,13] or the nuclear spin of the impurity-near-neighbor host atoms relevant for the satellite NMR measurements.[16,17] We are interested in inquiring what would be the influence of the dissipative dynamics of $\mathbf{S}$ on the spin dynamics of I. It is clear that the Hamiltonian in (6) minus the term proportional to J can be solved exactly as the conduction electrons do not couple to the impurity spin. If we treat the term proportional to J perturbatively the resulting analysis would yield the relaxation rates of the form (2) and (3). Here we take an alternate route and consider the Kondo Hamiltonian with an anisotropic exchange interaction with two components $J_{\parallel}$ and $J_{\perp}$:

$$\mathcal{H}_K=\sum_{\mathbf{k},\sigma}\varepsilon(\mathbf{k})c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}-J_{\parallel}S_z\sum_{\mathbf{k},\mathbf{k}'}(c^{\dagger}_{\mathbf{k}'\uparrow}c_{\mathbf{k}\uparrow}-c^{\dagger}_{\mathbf{k}'\downarrow}c_{\mathbf{k}\downarrow})-J_{\perp}\sum_{\mathbf{k},\mathbf{k}'}(S_{+}c^{\dagger}_{\mathbf{k}'\downarrow}c_{\mathbf{k}\uparrow}-S_{-}c^{\dagger}_{\mathbf{k}'\uparrow}c_{\mathbf{k}\downarrow})\ . \tag{7}$$

This Hamiltonian can be represented in terms of spin-density and charge-density excitations which are bosonic in nature (see, e.g., Refs. 20 and 21). The charge-density excitations completely drop out of the problem leading finally to the following form of the Kondo Hamiltonian:

$$\mathcal{H}_K=\hbar v_F\sum_{k>0}ka^{\dagger}_{\mathbf{k}}a_{\mathbf{k}}+\frac{J_{\parallel}}{2}S_z\sum_{k>0}e^{-k/2k_c}\sqrt{k/\pi L}\,(a^{\dagger}_{\mathbf{k}}+a_{\mathbf{k}})+\frac{J_{\perp}k_c}{2\pi}(S_{+}e^{\xi}+S_{-}e^{-\xi})\ , \tag{8}$$

where $a^{\dagger}_{\mathbf{k}}$, $a_{\mathbf{k}}$ are the *Bose* operators for spin-density excitations, k_c is a cutoff related to D, v_F is the Fermi velocity, and

$$\xi=\sum_{k>0}e^{-k/2k_c}\sqrt{4\pi/kL}\,(a_{\mathbf{k}}-a^{\dagger}_{\mathbf{k}})\ . \tag{9}$$

We now make a unitary transformation $R^{-1}\mathcal{H}R$ with

$$R=\exp(S_z\xi)\ , \tag{10}$$

which results in

$$\begin{aligned}\mathcal{H}'&=R^{-1}\mathcal{H}R\\&=AI_zS_z+\hbar\omega_N I_z+\hbar\omega_e S_z+\frac{J_{\perp}k_c}{2\pi}S_x\\&\quad+\left[\frac{J_{\parallel}}{2\pi\hbar v_F}-2\right]\hbar v_F S_z\sum_{k>0}e^{-k/2k_c}\sqrt{\pi k/L}\,(a_{\mathbf{k}}+a^{\dagger}_{\mathbf{k}})\\&\quad+\hbar v_F\sum_{k>0}ka^{\dagger}_{\mathbf{k}}a_{\mathbf{k}}\ .\end{aligned} \tag{11}$$

For convenience we use the following compact notations:

$$G_k = -\hbar\sqrt{K\pi v_F\omega_{\mathbf{k}}/L}\,e^{-\omega_{\mathbf{k}}/2\omega_c} , \tag{12}$$

where we have introduced frequency variables $\omega_{\mathbf{k}} = v_F k$, $\omega_c = v_F k_c$, and

$$\Delta = \frac{J_\perp k_c}{2\pi\hbar} , \tag{13a}$$

$$K = \left[1 - \frac{J_\parallel}{4\pi\hbar v_F}\right]^2 . \tag{13b}$$

Further denoting $\rho = (2\pi\hbar v_F)^{-1}$ as the density of states at the Fermi surface, Eqs. (13) can be cast in a dimensionless form

$$\begin{aligned} \Delta/\omega_c &= -\rho J , \\ K &= \left[1 - \frac{1}{2}\rho J\right]^2 . \end{aligned} \tag{14}$$

The Hamiltonian in (11) can now be written as,

$$\begin{aligned} \mathcal{H}' = {} & AI_zS_z + \hbar\omega_N I_z + \hbar\omega_e S_z + \hbar\Delta S_x \\ & + 2S_z \sum_{\mathbf{k}} G_{\mathbf{k}}(a_{\mathbf{k}} + a_{\mathbf{k}}^\dagger) + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} . \end{aligned} \tag{15}$$

The Hamiltonian in (15), sans the first two terms, is identical to the spin-boson Hamiltonian recently studied at great length by Leggett *et al.*[21] Earlier, we treated a similar but simpler Hamiltonian in the context of the dynamics of an impurity spin coupled to a spin-boson dissipative system.[22] The present calculation thus proceeds along similar lines. It has been shown by us, amongst others, that a convenient perturbative treatment of the spin-bath coupling is possible upon making a unitary transformation on the Hamiltonian:[23]

$$\tilde{\mathcal{H}} = T\mathcal{H}'T^{-1} , \tag{16}$$

where T is a unitary operator defined by

$$T \equiv \exp\left[-2S_z \sum_{\mathbf{k}} (G_{\mathbf{k}}/\hbar\omega_{\mathbf{k}})(a_{\mathbf{k}} - a_{\mathbf{k}}^\dagger)\right] . \tag{17}$$

Thus we obtain

$$\begin{aligned} \tilde{\mathcal{H}} = {} & AI_zS_z + \hbar\omega_{\mathrm{N}} I_z + \hbar\omega_e S_z \\ & - \hbar\Delta(B_+S_- + B_-S_+) + \sum_{\mathbf{k}} \hbar\omega_k a_{\mathbf{k}}^\dagger a_{\mathbf{k}} , \end{aligned} \tag{18}$$

where $S_\pm = S_x \pm iS_y$ and

$$B_\pm = \exp\left[\pm 2\sum_k (G_k/\hbar\omega_k)(a_k - a_k^\dagger)\right] . \tag{19}$$

In arriving at (18) from (8) we have omitted certain constant terms as they do not contribute to the dynamics.

The central quantity of interest is the correlation function

$$C(t) = \mathrm{Tr}[\tilde{\rho} I_x(0) I_x(t)] , \tag{20}$$

where $\tilde{\rho}$ is the canonical equilibrium density operator and the time dependence of I_x is governed by the full Hamiltonian $\mathcal{H}$ in Eq. (6). As both the operators R and T commute with **I**, the Laplace transform of $C(t)$ in (20) may be written in terms of $\tilde{\mathcal{H}}$ as[24]

$$\hat{C}(p) = \mathrm{Tr}_S\{\rho_S I_x[\hat{U}(p)]_{\mathrm{av}} I_x\} . \tag{21}$$

In writing (21) we have used the Liouville operator formalism for introducing the bath-averaged time development operator $[\hat{U}(p)]_{\mathrm{av}}$, where $U(p) = 1/(p - iL)$, L being the Liouvillian associated with $\tilde{\mathcal{H}}$. In addition we have factorized the canonical density matrix $\tilde{\rho}$, assuming the system-bath interaction to be smaller than thermal energy, as $\tilde{\rho} \approx \rho_S \cdot \rho_B$, where ρ_S is the density operator for the spin system, associated with the first three terms in (18), and ρ_B is the density matrix for a bath of noninteracting bosons, the Hamiltonian of which is given by the last term in (18). The bath-averaged time development operator contains all the information regarding the influence of the electronic environment on the impurity atom. For notational convenience we introduce a frequency variable for the hyperfine constant: $a = A/\hbar$.

B. Resolvent expansion

The strategy now is to treat the term proportional to $\rho J_\perp$ perturbatively. We separate the Hamiltonian in (18) into $\mathcal{H}_S$, $\mathcal{H}_I$, and $\mathcal{H}_B$, where

$$\begin{aligned} \mathcal{H}_S &= AI_zS_z + \tfrac{1}{2}\hbar\omega_N I_z + \hbar\omega_e S_z , \\ \mathcal{H}_I &= -\hbar\Delta(B_+S_- + B_-S_+) , \\ \mathcal{H}_B &= \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} . \end{aligned} \tag{22}$$

At this stage we wish to reemphasize the fact that the steps leading from (8) to (22) are exact except for neglecting an additive constant term. The quantity crucial for calculating the correlation function (20) is the bath-averaged time development operator which in its exact form can be written as $[U(p)]_{\mathrm{av}} = \mathrm{Tr}_B[\rho_B \cdot 1/(p - iL)]$. The approximation comes in when we treat H_I as a perturbation so that, to second order in H_I, the Laplace transformed bath-averaged time development operator reads[24]

$$[\hat{U}(p)]_{\mathrm{av}} \approx \frac{1}{p - iL_S + [L_I(p - iL_S - iL_B)^{-1}L_I]_{\mathrm{av}}} , \tag{23}$$

where L_S, L_I, and L_B are Liouville operators associated with $\mathcal{H}_S$, $\mathcal{H}_I$, and $\mathcal{H}_B$, respectively. Denoting the states of I by the latin indices m and m' and those of S by the Greek indices μ and ν, (21) may be written as

$$\begin{aligned} \hat{C}(p) = {} & \sum_{mm'} |\langle m'|I_x|m\rangle|^2 \\ & \times \sum_{\nu\nu'} \langle m\nu|\rho_S|m\nu\rangle \\ & \times (m\nu, m'\nu|[\hat{U}(p)]_{\mathrm{av}}|m\nu', m'\nu') . \end{aligned} \tag{24}$$

The "states" of the Liouville operators are denoted by $|\nu\mu)$. For simplicity we consider the case $I = \frac{1}{2}$ so that only the terms with $m = -m'$ survive in (24), which means that a relevant matrix element of the operator $(p-iL_S)$ has the form

$$(m\mu,-m\nu|(p-iL_S)|m\mu,-m\nu)$$
$$=p-2im\omega_N-ima(\mu+\nu)/2-i\omega_e(\mu-\nu)/2\ . \tag{25}$$

Equation (25) indicates that the expressions to be obtained later may be written in a compact form by introducing the notation

$$s=p-2im\omega_N\ . \tag{26}$$

With this in mind the matrix of the self-energy given in (23) can be evaluated explicitly and a typical element is given by

$$\begin{aligned}(m\mu,-m\nu|&\left[L_I\frac{1}{p-iL_S-iL_B}L_I\right]_{\text{av}}|m\mu',-m\nu')\\ &=(1/\hbar^2)\sum_{n,n'}\langle n|\rho_B|n\rangle\left[\delta_{\nu\nu'}\sum_{\eta}\frac{\langle\mu n|\mathcal{H}_I|\eta n'\rangle\langle\eta n'|\mathcal{H}_I|\mu' n\rangle}{s-i(E_n-E_{n'})/\hbar-i\omega_e(\eta-\nu)-iam(\eta+\nu)}\right.\\ &\qquad+\delta_{\mu\mu'}\sum_{\eta}\frac{\langle\nu' n|\mathcal{H}_I|\eta n'\rangle\langle\eta n'|\mathcal{H}_I|\nu n\rangle}{s-i(E_{n'}-E_n)/\hbar-i\omega_e(\mu-n)-iam(\mu+\eta)}\\ &\qquad-\frac{\langle\mu n|\mathcal{H}_I|\mu' n'\rangle\langle\nu' n'|\mathcal{H}_I|\nu n\rangle}{s-i(E_{n'}-E_n)/\hbar-i\omega_e(\mu'-\nu)-iam(\mu'+\nu)}\\ &\qquad\left.-\frac{\langle\mu n|\mathcal{H}_I|\mu' n'\rangle\langle\nu' n'|\mathcal{H}_I|\nu n\rangle}{s-i(E_n-E_{n'})/\hbar-i\omega_e(\mu-\nu')-iam(\mu+\nu')}\right],\end{aligned} \tag{27}$$

where E_n denotes the eigenvalue of the bath Hamiltonian $\mathcal{H}_B$. We note that the matrix for $\{p-iL_S+[L_I(p-iL_S-iL_B)^{-1}L_I]_{\text{av}}\}$, for a fixed m and within the subspace of S, is block diagonal with 2×2 blocks. However, we need focus only on the upper left block as is evident from (24), and thus we find (displaying only the upper left block) for the matrix of $[\hat{U}(p)]_{\text{av}}$:

$$\frac{1}{\text{Det}(m)}\begin{bmatrix} s+iam+\hat{\Phi}_{+-}(s_-)+\hat{\Phi}'_{+-}(s_+) & \hat{\Phi}_{-+}(s_+)+\hat{\Phi}'_{-+}(s_-)\\ \hat{\Phi}_{+-}(s_-)+\hat{\Phi}'_{-+}(s_+) & s-iam+\hat{\Phi}_{-+}(s_+)+\hat{\Phi}_{-+}(s_-)\end{bmatrix}, \tag{28}$$

where $s_\pm=s\pm i\omega_e$ and $\text{Det}(m)$ is given by

$$\begin{aligned}\text{Det}(m)=s^2&+s[\hat{\Phi}_{+-}(s_-)+\hat{\Phi}_{-+}(s_+)]\\ &+[\hat{\Phi}'_{+-}(s_+)+\hat{\Phi}'_{-+}(s_-)]+\tfrac{1}{4}a^2\\ &+iam\{[\hat{\Phi}_{-+}(s_+)+\hat{\Phi}'_{-+}(s_-)]\\ &\qquad-[\hat{\Phi}_{+-}(s_-)+\hat{\Phi}'_{+-}(s_+)]\}\ .\end{aligned} \tag{29}$$

In (28) and (29)

$$\Phi_{\pm\pm}(t)=\frac{\hbar^2}{4}\langle B_\pm(0)B_\pm(t)\rangle_B\ , \tag{30}$$

and primed quantities have t replaced by $-t$. The hat denotes the Laplace transform.

The bath correlation functions $\Phi_{\pm\pm}(t)$ can be explicitly evaluated because the required density matrix involves the Hamiltonian of the bath alone. Within the Ohmic dissipation model, and for $\hbar\beta$, $|t|\gg 1/\omega_c$ the bath correlation functions in (30) yield[23]

$$\begin{aligned}\Phi_{+-}(t)&=\Phi_{-+}(t)\\ &\equiv\Phi(t)=\frac{1}{4\hbar^2}\exp[i\pi K\text{sgn}(t)]\\ &\qquad\times\left[\frac{\pi}{\hbar\beta\omega_c}\right]^{2K}\frac{1}{[\sinh(\pi|t|/\hbar\beta)]^{2K}}\ .\end{aligned} \tag{31}$$

The Laplace transform of (31) finally takes the form

$$\begin{aligned}\hat{\Phi}(p)&=\tfrac{1}{4}F(p)\exp(i\pi K),\\ \hat{\Phi}'(p)&=\tfrac{1}{4}F(p)\exp(-i\pi K)\ ,\end{aligned} \tag{32}$$

where

$$F(p)=(\Delta^2/\omega_c)(2\pi k_B T/\hbar\omega_c)^{2K-1} \times B(1-2K,K+p\hbar\beta/2\pi) \ , \tag{33}$$

B in (33) denoting Euler's complex β function.

C. Result for the NMR line-shape function

With the time development operator available one can calculate the correlation function using (24), which takes the form

$$\hat{C}(p)=\sum_{m,v,v'}\frac{1}{4}\frac{1}{Z_S}\exp[\hbar\beta(mav+\omega_N m-\omega_e v)] \times(-mv,mv|[\hat{U}(p)]_{\text{av}}|-mv',mv') \ . \tag{34}$$

Knowledge of $\hat{C}(p)$ is adequate for evaluating the NMR line shape within the linear response theory. It is worth mentioning that with the bath-averaged time development operator $[\hat{U}(p)]_{\text{av}}$ known, it is straightforward to also calculate the Mössbauer line shape but we restrict the present discussion to NMR experiments. The correlation function in its final form reads

$$\hat{C}(p)=\sum_m \frac{\exp(\hbar\omega_{\text{N}}\beta m)}{8\cosh(\frac{1}{2}\hbar\omega_N\beta)}\frac{s+\{F(s_+)+F(s_-)\}\cos(\pi K)/2-im(a/2)\tanh[\hbar\beta(ma-\omega_e)/2)]}{s[s+\{F(s_+)+F(s_-)\}\cos(\pi K)/2]-ma\{F(s_+)-F(s_-)\}\sin(\pi K)/2+a^2/4} \ . \tag{35}$$

Equation (35) describes the complete NMR line shape of a nucleus in the vicinity of a Kondo impurity spin. As one is normally interested in the line shape near the resonance frequency the *electronic* spin-relaxation rate can be directly read from (35) as

$$\gamma=\text{Re}\{F(i\omega_{0+})+F(i\omega_{0-})\}\cos(\pi K)/2 \ , \tag{36}$$

where ω_0 is the resonance frequency minus ω_{N} (ω_{N} is expected to be the resonance frequency in the absence of the hyperfine field). The electronic spin-relaxation rate being large in Kondo systems, one should divide the numerator and the denominator of (35) by $s+\{F(s_+)+F(s_-)\}\cos(\pi K)/2$ in order to extract the nuclear-spin-relaxation rate. The resulting expression has the form

$$s+\frac{a^2/4-ma\{F(i\omega_{0+})-F(i\omega_{0-})\}\sin(\pi K)/2}{i\omega_0+\{F(i\omega_{0+})+F(i\omega_{0-})\}\cos(\pi K)/2} \ . \tag{37}$$

For a nuclear spin relaxing with a rate Γ and under the influence of a static field the corresponding expression looks like $p-i\omega_H+\Gamma$. With this in mind it is straightforward to identify the effective hyperfine field as

$$\omega_{\text{hf}}=\frac{a\,\text{Im}\{F(i\omega_{0+})-F(i\omega_{0-})\}\sin(\pi K)/2\,\text{Re}\{F(i\omega_{0+})+F(i\omega_{0-})\}\cos(\pi K)/2}{\omega_0^2+[\text{Re}\{F(i\omega_{0+})+F(i\omega_{0-})\}\cos(\pi K)/2]^2} \ . \tag{38}$$

In the following analysis K will be written as $(1-\rho J_{\parallel}/2)^2\equiv 1-\varepsilon$, so that the parameter $\varepsilon=\rho J_{\parallel}-\frac{1}{4}(\rho J_{\parallel})^2$, and the cutoff $\hbar\omega_c$ may be denoted by D in order to follow notational conventions. Equation (36) describes the relaxation rate of impurity electronic spin and is applicable to NMR, Mössbauer, and even ESR experiments. Equation (38) represents the effective field acting on the nucleus and can be used to interpret the NMR Knight shift and Mössbauer hyperfine field measurements. We should emphasize that the separation of the exchange constant J into two components was made only as a formal mathematical procedure which by no means implies that $J_{\perp}$ is smaller than $J_{\parallel}$ (see also Ref. 10). Consequently on physical grounds, we shall treat $\rho J_{\perp}=\rho J_{\parallel}\equiv\rho J$ in the subsequent discussion.

III. ESR LINE SHAPE: TRANSVERSE SUSCEPTIBILITY OF THE IMPURITY SPIN

The analysis till now yielded the longitudinal relaxation rate of the impurity spin. In order to interpret an ESR experiment wherein the probe participates directly in the relaxation process we have to calculate the imaginary part of the transverse dynamical susceptibility. A theoretical calculation for the T_2 relaxation rate and the g shift was done by von Spalden *et al.* to explain their ESR data.[15] The analysis was quite unsatisfactory in view of the widely divergent values of T_K obtained from the relaxation rate and the g shift. Here we present a treatment which we think is superior in the sense that the Kondo divergence is removed and $J_{\parallel}$ is treated exactly.

For the ESR case we neglect the hyperfine interaction which is in any case not relevant for the specific experimental system at hand in which the nuclear spin is zero. In an ESR experiment one normally assumes the external field to point along the z axis so that the Hamiltonian for a Kondo impurity looks like

$$\mathcal{H}_{\text{ESR}}=\hbar\omega_e S_z-J\mathbf{S}\cdot\mathbf{s}(0)+\sum_{\mathbf{k},\sigma}\epsilon(\mathbf{k})c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} \ , \tag{39}$$

which is, in fact, just the Kondo Hamiltonian in an external field. One may then go about our earlier route of splitting the exchange constant into $J_{\parallel}$ and $J_{\perp}$ and calculate the ESR line shape within the linear-response theory, using the relation

$$I_{\mathrm{ESR}}(\omega)=\mathrm{Re}\int_0^{\infty}e^{-pt}\langle S_x(0)S_x(t)\rangle dt\ , \tag{40}$$

where the microwave field is applied along the x axis. In order to directly adapt our earlier derived results to the present case we assume now the external magnetic field to point along x axis and the microwave along the z axis, which is perfectly justified as the exchange coupling is isotropic in our final analysis. The Hamiltonian then has the form

$$\mathcal{H}_{\mathrm{ESR}}=\hbar\omega_e S_x-J\mathbf{S}\cdot\mathbf{s}(0)+\sum_{\mathbf{k},\sigma}\epsilon(\mathbf{k})c_{\mathbf{k}\sigma}^{\dagger}c_{\mathbf{k}\sigma}\ . \tag{41}$$

Accordingly the ESR line shape is given by

$$I_{\mathrm{ESR}}(\omega)=\mathrm{Re}\int_0^{\infty}e^{-pt}\langle S_z(0)S_z(t)\rangle dt\ . \tag{42}$$

We now repeat the procedure which led to Eq. (18) from Eq. (6), for our Hamiltonian in (41). The resulting transformed Hamiltonian reads

$$\begin{aligned}\tilde{\mathcal{H}}_{\mathrm{ESR}}=&\hbar\omega_e(B_+e^{\xi}S_-+B_-e^{-\xi}S_+)\\&-\tfrac{1}{2}\hbar\Delta(B_+S_-+B_-S_+)+\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}\ ,\end{aligned} \tag{43}$$

where all the quantities have already been introduced. The first two terms can now be treated perturbatively within the resolvent expansion formalism. The calculation proceeds exactly on the lines of Ref. 23 except for the evaluation of the bath correlation functions, which is a bit more complicated in this case. We skip the details, which would have been almost a repetition of Sec. II in any case, and just display the result for the ESR line shape:

$$I_{\mathrm{ESR}}(\omega)=\mathrm{Re}\frac{1}{p+G(p)}\ . \tag{44}$$

In order to extract the relaxation rate and the effective field we replace p in the relaxation function $G(p)$ by the approximate resonant absorption frequency ω_e. It can then be represented in terms of Euler's complex γ functions as follows:

$$\begin{aligned}G=&-\frac{2\pi k_B}{\hbar}(\rho J_{\perp})^2(T/\Lambda)^{-2\varepsilon}\frac{\Gamma(2\varepsilon-1)\Gamma(1-\varepsilon+i\Theta/T)}{\Gamma(1+\varepsilon+i\Theta/T)}(i\Theta+\varepsilon T)\cos\pi\varepsilon\\&+\frac{2\pi k_B}{\hbar}\Theta^2(T/\Lambda)^{2\eta}\frac{\cos\pi\eta}{i\Theta+\eta T}\frac{\Gamma(1-2\eta)\Gamma(1+\eta+i\Theta/T)}{\Gamma(1-\eta+i\Theta/T)}\\&+\frac{2\pi k_B}{\hbar}\frac{\rho J\Theta}{(2\pi)^2}(T/\Lambda)^{1-2\delta}\frac{\cos\pi\delta}{i\Theta/T-\delta}\frac{\Gamma(1+2\delta)\Gamma(1-\delta+i\Theta/T)}{\Gamma(1+\delta+i\Theta/T)}\ ,\end{aligned} \tag{45}$$

where $\eta=(\rho J_{\parallel})^2/4$, $\delta=(\rho J_{\parallel})/2-(\rho J_{\parallel})^2/4$, $\Lambda=\hbar\omega_c/2\pi k_B$, and we have introduced a new "Larmor temperature" $\Theta=\hbar\omega_e/2\pi k_B$. The real part of G in (45) is the *transverse* relaxation rate of the impurity spin and the imaginary part is the effective field acting on it:

$$\begin{aligned}\gamma_T&=\mathrm{Re}G\\h_{\mathrm{eff}}&=\mathrm{Im}G\ \cdot\end{aligned} \tag{46}$$

The results (46) can be used to interpret the relaxation and g-shift data in an ESR experiment. Again, in the following analysis we consider $\rho J_{\perp}=\rho J_{\parallel}=\rho J$.

IV. ANALYSIS OF RESULTS AND FIT TO EXPERIMENTAL DATA

A. The case of zero coupling with conduction electrons

In order to make a consistency check on results (35) and (45), we first investigate the specific case wherein the exchange interaction with the conduction electrons is zero. This can be achieved by taking the limit $\rho J\rightarrow 0$ in which case $F(p)$ vanishes. The resulting expression reads

$$\begin{aligned}\hat{C}(p)=&\frac{1}{4}\sum_m\exp\frac{(\hbar\omega_N\beta m)}{2\cosh(\frac{1}{2}\hbar\omega_{\mathrm{N}}\beta)}\\&\times\frac{s-im(a/2)\tanh(\hbar(ma-\omega_e)\beta/2)}{s^2+a^2/4}\ .\end{aligned} \tag{47}$$

The validity of this result can be easily checked if the correlation function were calculated using the Hamiltonian $\mathcal{H}_S=AI_zS_z+\hbar\omega_N I_z+\hbar\omega_e S_z$.

A similar procedure on (44) leads to

$$I_{\mathrm{ESR}}(\omega)=\mathrm{Re}\frac{1}{p-i\omega_e}\ , \tag{48}$$

which again can be obtained directly from the Hamiltonian of a free spin in a magnetic field. The effective field on the spin, from which one can extricate the value of the g shift, reduces to the external field as the exchange interaction has gone to zero.

B. The spin-relaxation rate

The longitudinal (T_1) relaxation rate described by (36) has quantities such as $\omega_0+\omega_e$ in the argument of the function $F(p)$. In the NMR case, ω_0 can be neglected in comparison to ω_e (the nuclear magneton being much smaller than the Bohr magneton) such that $F(\pm i\omega_e)$ is the relevant quantity in the expression for the relaxation rate. For simplifying subsequent analysis we use the notations introduced in (45), and represent the relaxation rate in terms of a function $F_\pm \equiv \alpha F(\pm i\Theta)$, which may be written as

$$F_\pm = \alpha(\rho J)^2 T^{-2\varepsilon} \frac{\Gamma(2\varepsilon-1)\Gamma(1-\varepsilon\pm i\Theta/T)}{\Gamma(1+\varepsilon\pm i\Theta/T)}(\pm i\Theta+\epsilon T) , \tag{49}$$

where $\alpha = \Lambda^{2\epsilon}(2\pi k_B/\hbar)$. This expression is substituted in (36) for obtaining the T_1 relaxation rate. A further expansion in a Taylor series in ρJ yields

$$\gamma \approx \frac{\pi k_B}{\hbar}(\rho J)^2[1-2\rho J \ln(T/\Lambda)+\cdots] , \tag{50}$$

which exactly matches the result quoted in (3).

At very low temperatures ($A/\varepsilon \gg k_B T$) in the context of a Mössbauer experiment, Gonzalez-Jimenez, Imbert, and Hartmann-Boutron,[11] showed that the electronic relaxation rate saturates and the Kondo correction becomes $\rho J \ln(A/D)$. We analyze now the line-shape expression (35) in the limit $T \rightarrow 0$. Because ε is much smaller than Θ/T one can make the following approximation:

$$\begin{aligned}\frac{\Gamma(1+i\Theta/T-\varepsilon)}{\Gamma(i\Theta/T+\varepsilon)} &= \exp[\ln\Gamma(1+i\Theta/T-\varepsilon) \\ &\quad -\ln\Gamma(i\Theta/T+\varepsilon)] , \\ &\approx \exp[(1-2\varepsilon)\psi(i\Theta/T)] , \end{aligned} \tag{51}$$

where ψ represents Euler's digamma function. In the limit $T \rightarrow 0$, $\psi(i\Theta/T)$ is well approximated by $\ln(i\Theta/T)$, which leads to a dramatic vanishing of the temperature dependence of the line shape:

$$\begin{aligned}\lim_{T\rightarrow 0} F(i\Theta) &\approx \frac{\pi k_B}{\hbar}(\rho J)^2 (T/\Lambda)^{-2\varepsilon}\Gamma(2\varepsilon-1)(\Theta/T)^{1-2\varepsilon} \\ &\quad \times (i\Theta+\varepsilon T)\exp[i\pi(1-\varepsilon)] \\ &\approx -\frac{\pi k_B}{\hbar}(\rho J)^2(\Theta/\Lambda)^{-2\varepsilon} \\ &\quad \times \Gamma(2\varepsilon-1) i\Theta \exp(-i\pi\varepsilon) . \end{aligned} \tag{52}$$

To third order in ρJ the relaxation rate γ then takes the form

$$\gamma \approx (\pi k_B/\hbar)(\rho J)^2 T[1-2\rho J \ln(\Theta/\Lambda)] . \tag{53}$$

This is referred to as the "saturation" of the Kondo correction observed experimentally at very low temperatures.[11]

For fitting the theory to the experimentally measured relaxation rates in NMR and Mössbauer experiments we use the following equation:

$$\gamma = \alpha \, \mathrm{Re}(F_+ + F_-)\cos(\pi\varepsilon)/2 . \tag{54}$$

We have two fit parameters α and ρJ and the quantity Θ is calculated from the applied magnetic field in the NMR case. For this purpose we have used the experimental value of the magnetic moment $\mu_{\mathrm{eff}} = 2.74\mu_B$ for Cu:Fe (see Ref. 13 for details). We have fitted the equation to the impurity spin-relaxation rates measured in the satellite NMR experiments of Alloul[16] and Kanert, Mali, and Mehring[17] (see Figs. 1 and 2). The fit is very good and the value of ρJ comes out to be a bit larger than 0.2 which is normally assumed for the Cu:Fe system. In the Mössbauer case there is no external field which means that $F_+ = F_-$, hence ω_0 cannot be neglected from the argument of $F(p)$ and is replaced by $2\pi A/k_B$. The resulting equation is fitted to the most recent Mössbauer data obtained by Bonville *et al.*[12] (see Fig. 3). The fit is as

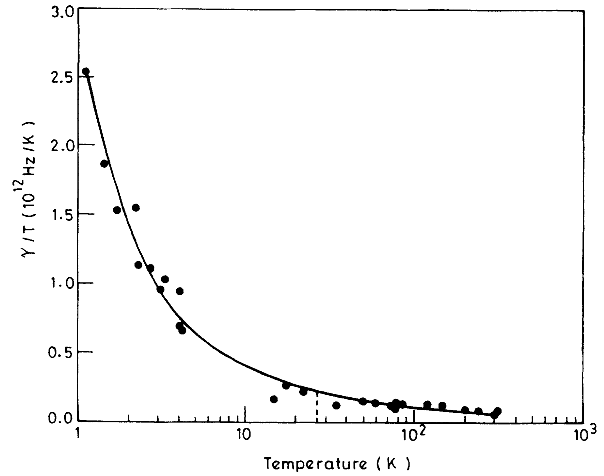

FIG. 1. The longitudinal relaxation rate γ fitted to the impurity spin-relaxation rates derived by Alloul (Ref. 16) from satellite NMR data on Cu:Fe. The error bars are not indicated in the figure. The field $\Theta = 0.9834$ and the best-fit line yields $\rho J = 0.28$ and $\alpha = 3.4$. The Kondo temperature for Cu:Fe is believed to be 27.6 K (Refs. 16, 17, and 26) and is indicated in the figures by a dotted line.

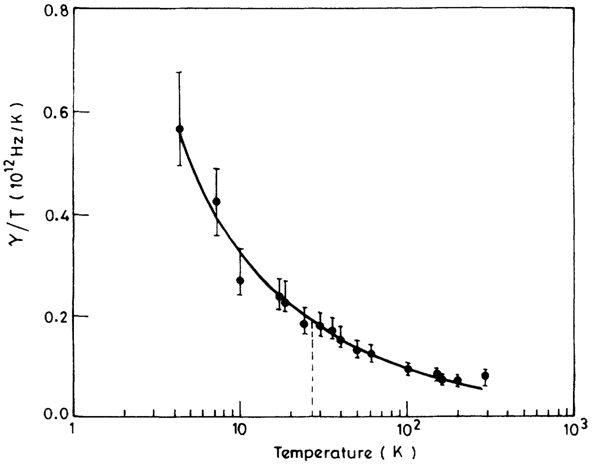

FIG. 2. The longitudinal relaxation rate γ fitted to the impurity spin-relaxation rates derived by Kanert, Mali, and Mehring (Ref. 17) from satellite NMR data on Cu:Fe. The field $\Theta = 0.9834$ and the best fit yields $\rho J = 0.28$ and $\alpha = 3.187$.

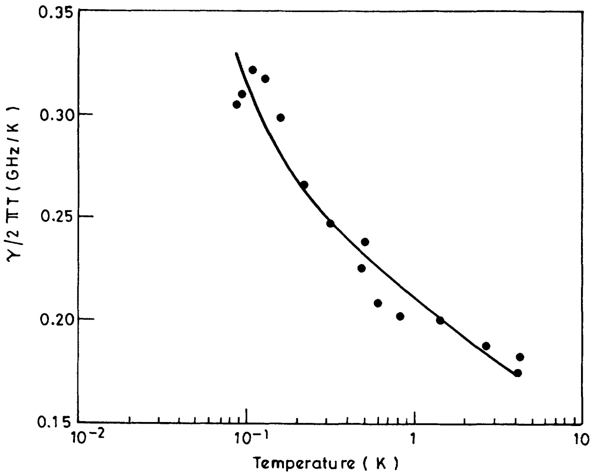

FIG. 3. The longitudinal relaxation rate γ fitted to the impurity spin-relaxation rates derived by Bonville *et al.* (Ref. 12) from Mössbauer experiments on Au:Yb. The external field Θ is zero, the hyperfine separation is 0.11 K, and the best fit yields $\rho J=0.069$ and $\alpha=7.821$. There is no general agreement over the value of T_K for Au:Yb but it is believed to be of the order of a few mK.

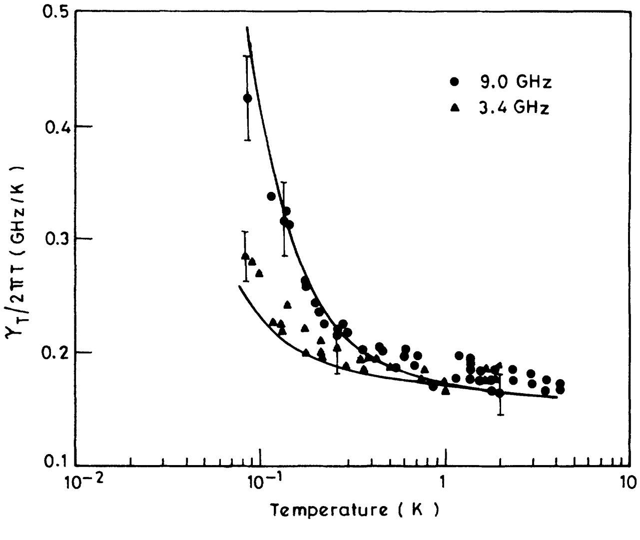

FIG. 4. The transverse relaxation rate γ_T fitted to the impurity spin-relaxation rates obtained by von Spalden *et al.* (Ref. 15) from ESR measurements on Au:^{174}Yb at two different values of the external field. Both fit lines are drawn using $\rho J=0.026$ and $\Lambda^{2\varepsilon}=2.961$ with only the external field taking different values corresponding to 9.0 and 3.4 GHz.

good as the one given by Abrikosov law used by the authors.

Shifting our attention to the *transverse* spin-relaxation rate (γ_T) given by (46), we find that it has a somewhat different structure from that of the longitudinal relaxation rate (γ). But the two results become identical for $\omega_e=0$, which is expected, as in the absence of an external magnetic field one cannot distinguish between transverse and longitudinal relaxation (provided, of course, one neglects the nuclear Zeeman and the hyperfine interaction terms from γ, being irrelevant in the ESR case). For Zeeman energies small compared to the temperature, the result for the transverse and longitudinal relaxation rates is the same up to third order in ρJ. Thus at high temperatures the T_1 and T_2 rates are equal for small ρJ. At low temperatures ($\rho J\cdot T \ll \Theta$) a similar expansion in ρJ shows that $\gamma \simeq 2\gamma_T$, i.e., the longitudinal relaxation is two times more effective than transverse relaxation.

In the fitting procedure we use $\gamma_T=\mathrm{Re}(G)$, where G is given by (45), with two fit parameters ρJ and Λ. Experimental data obtained by von Spalden *et al.*[15] have been used for the purpose (see Fig. 4). Again, Θ has been calculated from the applied external field and is *not* a fit parameter. The fit is satisfactory in the sense that the value of ρJ obtained from the relaxation-rate data is in good agreement with that obtained from the g-shift data (see Sec. IV D). The effect of the external magnetic field on the relaxation rate is clearly brought out in the low-temperature regime.

For the sake of comparison with the existing results widely used for data analysis we consider the *zero*-field relaxation rate

$$\gamma_0=\frac{2\pi k_B}{\hbar}(\rho J)^2(T/\Lambda)^{-2\varepsilon}\frac{\Gamma(2\varepsilon-1)\Gamma(1-\varepsilon)}{\Gamma(1+\varepsilon)}\varepsilon T\cos(\pi\varepsilon)\ . \tag{55a}$$

By defining an effective exchange constant $\tilde{J}(T)$ the above expression can be cast in a form similar to the second-order relaxation rate (2):

$$\gamma_0=\frac{\pi k_B}{\hbar}(\rho\tilde{J}(T))^2 T\ , \tag{55b}$$

where

$$\rho\tilde{J}(T)=\rho J(T/\Lambda)^{-\varepsilon}\sqrt{[2\Gamma(2\varepsilon-1)\Gamma(1-\varepsilon)/\Gamma(1+\varepsilon)]\varepsilon\cos(\pi\varepsilon)}\ . \tag{55c}$$

One can see that the effective exchange constant increases as the temperature decreases and should become infinite as $T \to 0$. This feature constitutes the essence of the Kondo problem. Note that $\tilde{J}(T)$ does not diverge at $T=T_K$ as in conventional perturbation theories. For small ρJ, $\tilde{J}(T)$ can be approximated by

$$\rho\tilde{J}(T)\approx\frac{\rho J}{(T/\Lambda)^{\rho J}}=\frac{\rho J}{1+\rho J\ln(T/\Lambda)+\cdots}$$
$$=\frac{1}{\ln(T/T_K)+O(\rho J)}\ , \tag{56}$$

which when substituted in (55b) leads to

$$\gamma_0 = \frac{\pi k_B}{\hbar} T \frac{1}{[\ln(T/T_K) + O(\rho J)]^2} , \tag{57}$$

where $T_K \equiv \Lambda \cdot \exp(-1/\rho J)$. If we neglect terms of order ρJ from the denominator of (57) we are left with the well-known Abrikosov law introduced earlier in (5). Thus, the Abrikosov law derived originally from a diagrammatic technique turns out to be a special case of the relaxation rate calculated by us.

C. The NMR Knight shift

The Knight-shift data had been analyzed till now by relating it to static susceptibility for which the Curie-Weiss form $1/(T+T_K)$ was assumed. With this method one cannot explain the saturation of the hyperfine field at low temperatures.[13,16,26] Moreover, the Curie-Weiss law can only be used in a limited temperature range as suggested by the experimental data[16] and also by the numerical calculation of Wilson.[18] On the other hand our expression for the hyperfine field given by (38) is valid even at very low temperatures and would saturate in the limit $T \to 0$, in view of (52). At temperatures such that $\gamma \gg \omega_0$, the expression simplifies to yield

$$\omega_{\mathrm{hf}} = \frac{a\,\mathrm{Im}\{F(i\omega_{0+}) - F(i\omega_{0-})\}}{\mathrm{Re}\{F(i\omega_{0+}) + F(i\omega_{0-})\}} \tan(\pi K)/2 . \tag{58}$$

One can easily verify that for high temperatures $(T \gg \Theta/\varepsilon)$ the expression (58) follows a Curie-Weiss law of the form $\omega_{\mathrm{hf}} \sim 1/T$.

For fitting the theory to experimental data we use the following fit equation with three fit parameters A_1, Ω, and ρJ:

$$\omega_{\mathrm{hf}} = A_1 \frac{\mathrm{Im}\{F_+ - F_-\}\sin(\pi K)/2 \cdot \mathrm{Re}\{F_+ + F_-\}\cos(\pi K)/2}{\Omega^2 + [\mathrm{Re}\{F_+ + F_-\}\cos(\pi K/2]^2} , \tag{59}$$

where A_1 and Ω arise from the freedom to choose the cutoff Λ and ω_0. For the high-temperature data one would need only two fit parameters. The parameter Θ as usual has been calculated from the applied external field which is typically 40–50 KGauss. We analyze the satellite NMR Knight-shift data of Alloul[16] and Boyce and Slichter,[26] and the Mössbauer hyperfine data of Steiner, Hüfner, and Zdrojewski[13] (see Figs. 5, 6, and 7). Note that the value of ρJ for Cu:Fe obtained from the hyperfine field analysis is in fair agreement with that obtained from the NMR relaxation data. Moreover, same parameter values are used to explain the low as well as high-temperature data. Although the number of adjustable parameters seems unsatisfactory at the first glance it is almost impossible to fit the data in the entire range of temperature with a fewer set of parameters (see, e.g., Ref. 13).

D. The g shift

The g shift in an ESR experiment is related to the effective field acting on the impurity spin in the following

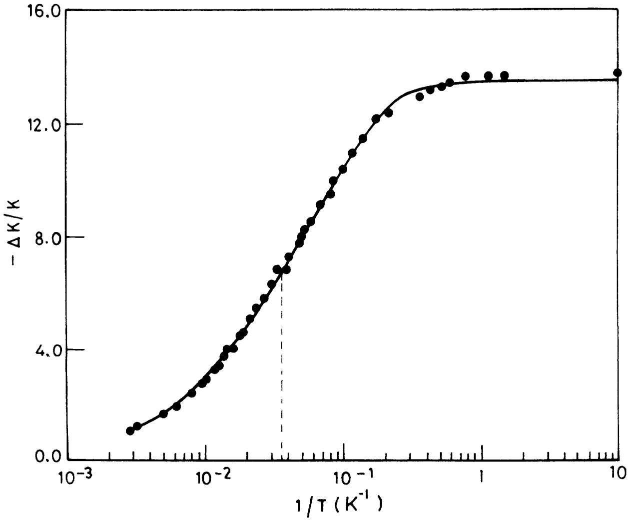

FIG. 5. The hyperfine field expression fitted to the relative NMR Knight shift which is conventionally denoted by $\Delta K/K$, measured by Alloul (Ref. 16) from satellite NMR experiments on Cu:Fe. The field $\Theta = 3.21$ and the best-fit line corresponds to $\rho J = 0.29$, $A_1 = 39.314$, and $\Omega = 1.67$.

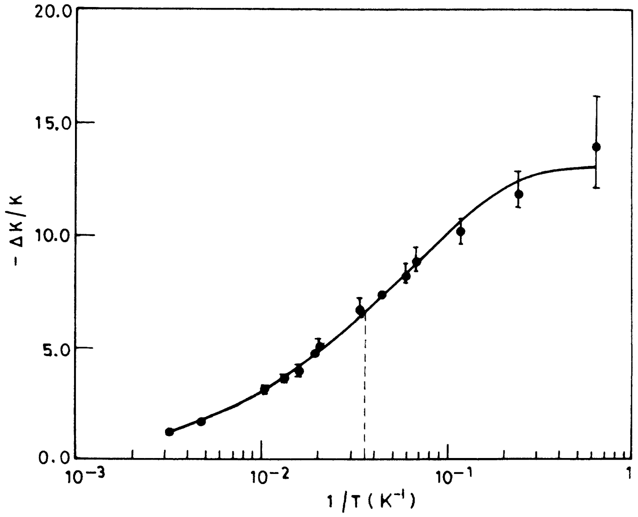

FIG. 6. The hyperfine field expression fitted to the relative NMR Knight shift measured by Boyce and Slichter (Ref. 26) from satellite NMR experiments. The data presented is for different field but for the fit Θ is taken to be 3.18. The best fit yields $\rho J = 0.25$, $A_1 = 43.92$, and $\Omega = 1.8654$.

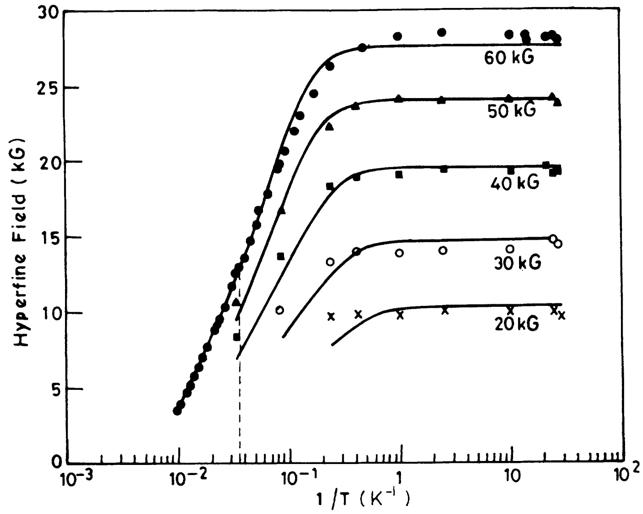

FIG. 7. The hyperfine field expression fitted to the hyperfine field measured in a Mössbauer experiment on Cu:Fe by Steiner, Hüfner, and Zdrojewski (Ref. 13). The fields are indicated in the figure and all curves are calculated using $\rho J = 0.28$ and $\Omega = 1.03$. However, A_1 varies with the field and takes values 46.69, 43.90, 39.35, 34.21, and 30.36 corresponding to the field of 60, 50, 40, 30, and 20 kG, respectively.

manner:[15]

$$h_{\text{eff}} = h_0(1 + \Delta g / g_0) \ , \tag{60}$$

where g_0 is the ionic g value and h_0 is the external field, Now, in expression (46) for h_{eff} given by the imaginary part of G, there are three different terms. The last term has a factor T/Λ which makes it much smaller than the other two terms, in view of the assumption $(\Lambda \gg T)$ made while writing down Eq. (31). For the time being therefore, we consider the imaginary part of only the first two terms of G, expanded for small ρJ. We discover that the leading term is equal to ω_e which corresponds to the applied field and thus the first term h_0 in (60). Up to second order in ρJ we may then extract

$$h_0 \cdot \Delta g / g_0 \approx \Theta \rho J [1 + 2\rho J \{ -\text{Re}\psi(1 + i\Theta/T) + \ln(T/\Lambda) + \psi(1) \}] \ , \tag{61}$$

where ψ represents Euler's digamma function. This expression can be manipulated to yield

$$h_0 \cdot \Delta g / g_0 \approx \frac{\Theta/2}{1/2\rho J + \text{Re}\psi(1 - i\Theta/T) - \ln(T/\Lambda) - \psi(1)} \ . \tag{62}$$

If one now sets $\Lambda \cdot \exp(-1/2\rho J) \equiv T_K$, the above result takes the form

$$h_0 \cdot \Delta g / g_0 \approx \frac{\Theta/2}{\ln(T_K/T) + \text{Re}\psi(1 - i\Theta/T) - \psi(1)} \ , \tag{63}$$

which exactly matches the result for the g shift derived by von Spalden *et al.* [Eq. (3) of Ref. 15]. Thus, one may conclude that the present treatment is of more general nature, the result of von Spalden *et al.* being one special case for small ρJ.

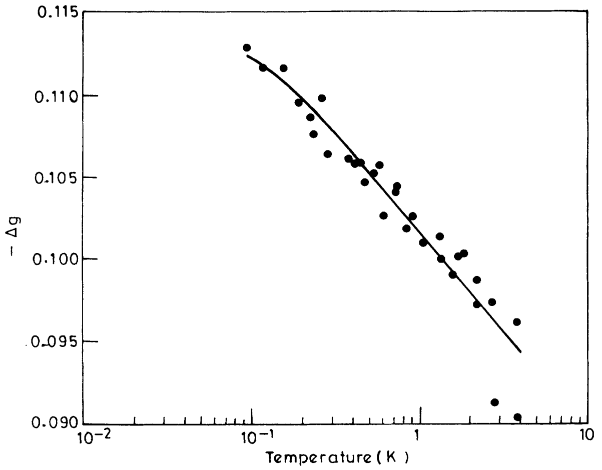

FIG. 8. The expression for $g_0(h_{\text{eff}}/\omega_e + 1)$ fitted to Δg measured by von Spalden *et al.* (Ref. 15) from an ESR study on Au:^{174}Yb. The ionic g value g_0 is assumed to be 3.423. The field corresponds to 9.0 GHz and the best fit line is drawn for $\rho J = 0.0268$ and $\Lambda^{2\varepsilon} = 1.804$.

We also analyze the g-shift data using the following fit equation with two adjustable parameters Λ and ρJ:

$$\Delta g / g_0 = \text{Im}(G)/\Theta + 1 \ . \tag{64}$$

The fit turns out to be quite good and the value of ρJ is in agreement with those obtained from the ESR relaxation data (see Fig. 8).

V. DISCUSSION AND CONCLUSIONS

We have derived expressions for the longitudinal impurity spin-relaxation rate and the hyperfine field from a common line-shape analysis, relevant for NMR and Mössbauer experiments. We have also obtained expressions for the transverse relaxation rate and the g shift, in the context of an ESR experiment, from a separate calculation. The entire analysis is based on a unified theoretical framework of a Hamiltonian that may be viewed as an extended version of the so-called spin-boson Hamiltonian, studied extensively in the context of dissipation in quantum two-state systems. In all our calculations the exchange constant $J_\parallel$ has been treated exactly in order to remove the Kondo divergence, while $J_\perp$ has been kept to second order. Treating the exchange term in the Kondo Hamiltonian (1) perturbatively means using the direct product of the impurity spin state and the electronic Fermi sphere state as the unperturbed wave function. This amounts to adiabatically decoupling the motion of the spin and that of the electrons. In such a situation, if the perturbation is dynamic and local, which is the case here, this approximation always leads to divergent results as is also exemplified by a heavy particle tunneling in a metallic environment.[25] One has to employ a nonadiabatic scheme in order to circumvent the problem. By treating $J_\parallel$ exactly we choose an unperturbed wave function where the state of the electrons depends on the state of the impurity spin, thereby taking the nonadiabaticity of the problem into account. Thus our treatment of the nonadiabaticity arising from the electron drag is able to remove the Kondo divergence which occurs in the adiabatic limit. Using the anisotropic form of the Kondo Hamiltonian has allowed us to recognize the fact that the term proportional to $J_{\parallel}$ does not cause impurity spin flips. The impurity spin flips are in fact caused by the term proportional to $J_{\perp}$. Since $J_{\perp}$ and $J_{\parallel}$ play different roles we feel some justification in treating them differently.

In the language of the spin-boson problem the second-order treatment of $J_{\perp}$ is equivalent to the so-called dilute-bounce-gas approximation (DBGA),[21,23] which has been found to be very good for describing dissipative tunneling in two-level systems. However, we should mention here that there have been some doubts regarding the validity of the DBGA in the Kondo regime.[21] This point needs a bit of discussion in order to assess the applicability of the preceding theoretical calculations to the Kondo problem, as done in the following paragraph.

The main strength of our analysis is the fact that the Kondo divergence, which plagues most calculations, has been eliminated and still we have been able to obtain analytical results. Furthermore recent quantum Monte Carlo (QMC) simulation of the spin-boson Hamiltonian by Egger and Weiss[27] provides some guidance regarding the validity of the DBGA in the Kondo regime. The QMC results quantitatively show that in the parameter regime where the spin-boson Hamiltonian can be related to the Kondo Hamiltonian, the DBGA is very good for all temperatures except below a temperature $T' \equiv \hbar\Delta/k_B(\Delta/\omega_c)^{K/(1-K)}$. In our notations this means $T'/\Lambda \equiv 2\pi(\rho J)^{1/\varepsilon}$. Below T' the QMC result deviates from the DBGA result *at long times.* This implies that our results become questionable at very low temperatures *and low frequencies.* But because of the fact that the external magnetic field is ubiquitous in NMR and ESR experiments the relaxation rate is not required at very low frequencies. Even in the Mössbauer relaxation measurements the relaxation rate is required at the hyperfine separation frequency which, in the case of Au:Yb, is about 0.11 K. Thus the results presented here can be confidently used to analyze spectroscopic data in Kondo systems. One consequence of the arguments presented above is that it would be grossly erroneous to calculate the zero field, *static* susceptibility of a Kondo spin from the DBGA result for the spin-boson Hamiltonian.[23]

In conclusion, using a self-consistent perturbation theory we have derived complete line-shape expressions relevant for NMR, Mössbauer, and ESR experiments in dilute magnetic alloys. The bosonized form of the conventional Kondo Hamiltonian has been used. Explicit analytical results are obtained for the longitudinal and transverse impurity spin-relaxation rates, the NMR Knight shift, and the ESR g shift. Although the exchange coupling is *formally* viewed to be anisotropic and the transverse component is treated perturbatively, our results contain J up to arbitrary orders. The approximation used is equivalent to the DBGA in the context of the spin-boson Hamiltonian. The Kondo divergences have been removed and the results are valid even at the so-called Kondo temperature. Several perturbative results extant in the earlier literature are recovered as special cases of the more general calculation presented here. The derived theoretical expressions have been used to analyze and interpret the experimental data reported by diverse experimental groups involved with NMR and Mössbauer relaxation measurements, NMR Knight-shift and Mössbauer hyperfine field measurements, ESR relaxation and g-shift measurements. The fits are so satisfactory that we feel we have been able to make theoretical advance in a well studied and important field of condensed-matter physics, at least as far as the resonance spectroscopy data are concerned. Our treatment has also brought the Kondo problem into the realm of a basic model of quantum dissipative system that has been applied to a variety of phenomena such as tunneling of defects in metals, macroscopic quantum coherence in superconducting quantum interference devices, electron transfer process in chemical reactions, etc.[21]

ACKNOWLEDGMENT

One of us (T.Q.) acknowledges useful discussions with Professor Deepak Kumar.

---

[1] P. D. Sacramento and P. Schlottmann, Phys. Rev. B **43**, 13 294 (1991).

[2] D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).

[3] T. Ishiguro, H. Kaneko, Y. Nogami, H. Ishimoto, H. Nishiyama, J. Tsukamoto, A. Takahashi, M. Yamamura, T. Hagiwara, and K. Sato, Phys. Rev. Lett. **69**, 660 (1992).

[4] B. A. Jones and C. M. Varma, Phys. Rev. Lett. **58**, 843 (1987); J. W. Rasul and P. Schlottmann, Physica B **186-188**, 334 (1993); Y. Shmizu and O. Sakai, *ibid.* **186-188**, 891 (1993); K. Ingersent, B. A. Jones, and J. W. Wilkins, Phys. Rev. Lett. **69**, 2594 (1992).

[5] A. M. Tvselick and P. G. Weigmann, Adv. Phys. **32**, 453 (1983); N. Andrei, K. Furuya, and H. Lowenstien, Rev. Mod. Phys. **55**, 331 (1983).

[6] J. Kondo, Prog. Theor. Phys. (Kyoto) **32**, 37 (1964); *Solid State Physics: Advances in Research and Applications,* edited by H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 183.

[7] M. B. Walker, Phys. Rev. **176**, 432 (1968); R. Orbach and H. J. Spencer, *ibid.* **179**, 690 (1969).

[8] A. A. Abrikosov, Physics **2**, 5 (1966).

[9] W. Götze and P. Schlottmann, J. Low Temp. Phys. **16**, 87 (1974).

[10] P. W. Anderson and G. Yuval, Phys. Rev. Lett. **23**, 89 (1969).

[11] F. Gonzalez-Jimenez, P. Imbert, and F. Hartmann-Boutron, Phys. Rev. B **9**, 95 (1974); F. Hartmann-Boutron, *ibid.* **10**, 2113 (1974); F. Gonzalez-Jimenez, F. Hartmann-Boutron, and P. Imbert, *ibid.* **10**, 2212 (1974).

[12] P. Bonville, P. Imbert, G. Jéhanno, F. Gonzalez-Jimenez, and F. Hartmann-Boutron, Phys. Rev. B **30**, 3672 (1984).

[13] P. Steiner, S. Hüfner, and W. v. Zdrojewski, Phys. Rev. B **10**, 4704 (1974).

[14] K. Baberschke and E. Tsang, Phys. Rev. Lett. **45**, 1512 (1980).

[15] Y. von Spalden, E. Tsang, K. Baberschke, and P. Schlottmann, Phys. Rev. B **28**, 24 (1983).

[16] H. Alloul, Physica **86-88B**, 449 (1977).

[17] O. Kanert, M. Mali, and M. Mehring, Solid State Commun. **21**, 1047 (1977).

[18] K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975); H. R. Krishna-Murthy, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **35**, 1101 (1975).

[19] A. Narath, K. C. Brog, and W. H. Jones, Jr., Phys. Rev. B **2**, 2618 (1970).

[20] F. Guinea, V. Hakim, and A. Muramatsu, Phys. Rev. B **32**, 4410 (1985); K. D. Schotte, Z. Phys. **230**, 99 (1970); P. Schlottmann, Phys. Rev. B **25**, 4815 (1982); M. Blume, V. J. Emery, and A. Luther, Phys. Rev. Lett. **25**, 450 (1970).

[21] A. J. Leggett, S. Chakravarty, M. P. A. Fisher, A. T. Dorsey, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).

[22] S. Dattagupta and T. Qureshi, Ber. Bunsenges. Phys. Chem. **95**, 433 (1991).

[23] S. Dattagupta, H. Grabert, and R. Jung, J. Phys.: Condens. Matter **1**, 1405 (1989).

[24] S. Dattagupta, *Relaxation Phenomena in Condensed Matter Physics* (Academic, New York, 1987).

[25] J. Kondo, *Fermi Surface Effects,* Springer Series in Solid-State Science Vol. 77 (Springer, Heidelberg, 1988).

[26] J. B. Boyce and C. P. Slichter, Phys. Rev. B **13**, 379 (1976).

[27] R. Egger and U. Weiss, Z. Phys. B **89**, 97 (1992).