R_-/R_+. The indirect overlap contribution is always such as to decrease $|\psi|$ at shell I through overlap with neighboring anion states, and this contribution increases in importance with increase in the relative anion size. Hence, for large R_-/R_+ the strong pressure dependence of the ion-ion overlap terms can even lead to a negative shell-I pressure shift, as in the case of LiCl.

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High-Field Nuclear Relaxation of ^{173}Yb in Dilute *Au*Yb Alloys: Evidence for Anisotropic Conduction-Electron Exchange*

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Relaxation rates of the ^{173}Yb nuclear resonance in *Au*Yb have been measured in the low-temperature local-moment regime ($\omega_e T_2^e \gg 1$). The measured rates can be accounted for by virtual transitions of the Yb^{3+} moment within the Γ_7 doublet caused by exchange interactions with host conduction electrons. The absence of significant contributions to the high-field ^{173}Yb relaxation rates from virtual transitions to the Γ_8 quartet requires an anisotropic form for the exchange.

The properties of localized magnetic moments in metals are strongly influenced by exchange coupling to the host conduction electrons. Although an isotropic form has usually been assumed for this interaction, in the presence of orbital degeneracy an anisotropic form may be more appropriate, especially for rare-earth ions.[1] For exchange arising from covalent mixing between $4f$ and conduction electrons, Coqblin and Schrieffer[2] have argued that the traditional isotropic Hamiltonian,

$$\mathcal{H}_{ex}^{iso} = -\mathcal{J}(g_J - 1)\vec{J}\cdot\sum_{\substack{kk'\\ \sigma\sigma'}} C_{\vec{k}'\sigma'}^{\dagger}\vec{\sigma}C_{\vec{k}\sigma}, \quad (1)$$

should be replaced by an anisotropic Hamiltonian which, in the present case, takes the form,[3]

$$\mathcal{H}_{ex}^{aniso} = -\sum_{\substack{kk'\\ MM'}} \mathcal{J}_{MM'} C_{k'M'}^{\dagger} C_M^{\dagger} C_{M'} C_{kM}, \quad (2)$$

where J is the rare-earth total angular momentum, σ is the conduction-electron spin, $C^{\dagger}$ (C) are creation (annihilation) operators for the itinerant and local-moment electrons, M labels the $2J+1$ rare-earth eigenstates of the (crystal-field + Zeeman) Hamiltonian, and, $\vec{k}\sigma$ and kM label plane-wave and partial-wave conduction-electron states, respectively. The eigenfunctions of the partial waves are identical to those of the rare earth. The anisotropic interaction (2) describes combined spin and orbital exchange scattering by a rare-earth moment in the limit of jj coupling. This coupling is applicable to $Ce^{3+}(4f^1, J=\frac{5}{2})$ and $Yb^{3+}(4f^{13}, J=\frac{7}{2})$ for which $\vec{j}=\vec{J}$. We also note that an anisotropic expression essentially equivalent to (2) has been derived by Huang-Liu, Ling, and Orbach[1] for atomic exchange between $4f$ electrons and $5d$-like screening electrons.

To date, the most convincing evidence in support of the anisotropic coupling is provided by

(i) Kondo anomalies observed[3] in many alloys containing Ce^{3+} impurities. Since both $g_J - 1$ and $\mathcal{J}$ are negative for the $J = \frac{5}{2}$ ground manifold of Ce^{3+}, the sign of the isotropic interaction is positive and a Kondo effect is not expected, in contrast to the anisotropic interaction which is always negative. (ii) Zero-field Mössbauer linewidth measurements for ^{170}Yb in *Au*Yb by Gonzalez-Jimenez, Cornut, and Coqblin[4] yielded local-moment relaxation rates that increase more rapidly with temperature above 10 K than can be explained by the isotropic interaction.

In this Letter, we demonstrate that the magnitude and field dependence of local-moment nuclear relaxation rates give direct information about the form of the exchange provided that (i) the lowest J manifold is split by crystal-field interactions, (ii) the relaxation rates are measured for applied-field strengths which are comparable to the separation Δ between the ground state and the first excited crystal-field level (i.e., $g\mu_B H \sim \Delta$), and (iii) only the ground state is thermally populated (i.e., $k_B T \ll \Delta$). A strongly polarized ($g\mu_B H/k_B T \gg 1$) local moment is therefore required, which also facilitates observation of the nuclear resonance. In this regime, the nuclear relaxation rates are determined by low-frequency ($\omega \sim 0$) transverse fluctuations of the local moment arising from virtual excitations under the combined influence of exchange and hyperfine interactions. One may then distinguish between excitations within the lowest crystal-field multiplet, split by the Zeeman interaction, and excitations to higher crystal-field levels. For the anisotropic Hamiltonian (2) these two contributions to the local-moment fluctuation amplitude add *incoherently*. The effect of the higher-lying crystal-field levels on the nuclear relaxation rates is therefore weaker than for the isotropic Hamiltonian (1) for which the two contributions add *coherently*. Another difference is the fact that $\mathcal{J}_{MM'}$ in (2) can have different magnitudes depending explicitly on the crystal-field levels M and M', while $\mathcal{J}$ in (1) is a constant.

Ytterbium dissolves in gold as a trivalent ($J = \frac{7}{2}$) ion. Magnetic susceptibility experiments[5,6] show that the crystal-field ground state is an isolated Γ_7 doublet ($\Delta \approx 80$–90 K). The negative g-shift of the Γ_7 ESR[7] shows that the exchange is dominated by covalent mixing, as expected on the basis of the small $4f^{13}$-$4f^{14}$ interconfigurational energy of ytterbium (i.e., in a one-electron description, the proximity of the $4f^{14}$ level to the Fermi level). Thermal broadening of the ESR has been analyzed[7] by using (1) giving $\langle(\mathcal{J}\rho)^2\rangle = 0.016$, where ρ is the density of conduction-electron states at the Fermi energy for one spin direction. Mössbauer relaxation rates[8] yield essentially the same value, $\langle(\mathcal{J}\rho)^2\rangle = 0.015$. Recently, Mössbauer linewidth measurements over a wide temperature range have been analyzed with (2) by Gonzalez-Jimenez, Cornut, and Coqblin[4] assuming the energy-dependent exchange proposed by Cornut and Coqblin,[3]

$$\mathcal{J}_{MM'} = \tfrac{1}{2}|V_{kf}|^2(E_M^{-1} + E_{M'}^{-1}), \tag{3}$$

where $E_M (< 0)$ is the interconfigurational energy relative to the Mth crystal-field level, and V_{kf} is the mixing matrix element appropriately averaged over the Fermi surface. They find $(\mathcal{J}_{00}\rho)^2 = 0.0035$, $(\mathcal{J}_{01}\rho)^2 = 0.0080$, and $(\mathcal{J}_{11}\rho)^2 = 0.0148$, where $M = 0$ denotes the Γ_7 level, and $M = 1$ denotes the Γ_6 and Γ_8 levels (taken as degenerate).

The nuclear resonance properties of the ^{173}Yb impurity are governed by the hyperfine interaction

$$\mathcal{H}_{\rm hf} = A\vec{\mathbf{I}}\cdot\vec{\mathbf{J}}, \tag{4}$$

which leads to a strong local field and, consequently, very high NMR frequencies (450–530 MHz) when the moment is polarized in the range of applied fields (65–120 kOe) used in our experiments. A single resonance is observed at 1.0–2.0 K, in agreement with the fast-relaxation limit $\omega_n T_1^e \ll 1$. From analysis of our frequency-versus-field data a hyperfine constant $A = 160.4(9) \times 10^{-20}$ erg, crystal-field splitting $\Delta(\Gamma_8$-$\Gamma_7) = 84.4(3.5)$ K, and the relative level ordering $\Delta(\Gamma_6$-$\Gamma_7) \geq \Delta(\Gamma_8$-$\Gamma_7)$ have been obtained.[9]

The ^{173}Yb transverse nuclear relaxation times (T_2) discussed here were measured in *Au*^{173}Yb single crystals by means of phase-coherent spin-echo techniques with $\vec{H} \| [100]$. Exponential spin-echo decays were observed in every case. The experimental T_2 values at 1.0 K are shown in Fig. 1 plotted against the square of the applied field. The relaxation rates are much too fast to be affected appreciably by direct hyperfine coupling to the conduction electrons; and we conclude that relaxation is dominated by fluctuations of the local moment. Experiments at 2.0 K confirm the linear temperature dependence of the nuclear rates expected for a polarized local moment.[10]

We wish to compare our experimental results with predictions of (1) and (2). The computation of the nuclear relaxation rates is carried out to the lowest order in $\mathcal{J}\rho$, according to local-moment fluctuation theory[10] suitably modified to take account of the excited crystal-field levels. The

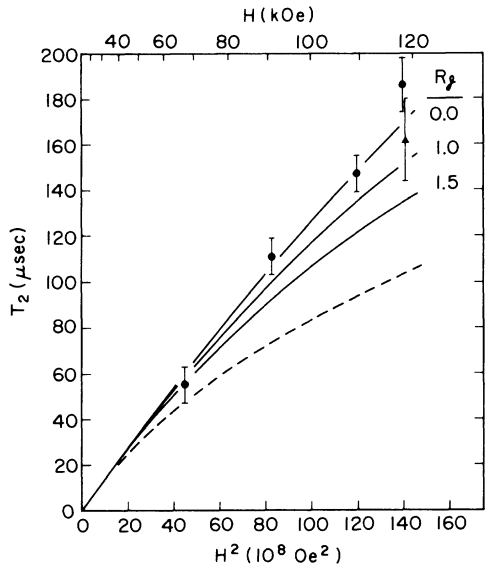

FIG. 1. ^{173}Yb transverse relaxation times plotted versus H^2 in 0.1 (●) and 0.05 (▲) at.% *Au*Yb single crystals at 1.0 K and $\vec{H}\|[100]$. The dashed curve was obtained with an isotropic exchange interaction using $(\mathcal{J}\rho)^2 = 0.016$. The solid curves were obtained with an anisotropic exchange interaction using $(\mathcal{J}_{00}\rho)^2 = 0.0035$ and indicated values for $R_{\mathcal{J}} \equiv \mathcal{J}_{01}/\mathcal{J}_{00}$.

transverse nuclear relaxation rate is given, in general, by

$$T_2^{-1} = T_{\|}^{-1} + \eta T_{\perp}^{-1}, \tag{5}$$

where $T_{\|}^{-1}$ and $T_{\perp}^{-1}$ are contributions from longitudinal and transverse fluctuations of the hyperfine field. The transverse term is enhanced by the factor η when only the central $(+\frac{1}{2} \longleftrightarrow -\frac{1}{2})$ transition is observed.[11,12] This correction is appropriate in the present case ($\eta = 17$ for $I = \frac{5}{2}$) because of strain- and field-induced quadrupole "wipeout" of the satellite transitions. Observation of the Γ_7 ESR shows that the low-temperature regime $\omega_e T_2^e \gg 1$ (where e refers to the electronic moment) applies in the present case. In this regime, the longitudinal fluctuations give a rate $T_{\|}^{-1} \propto \exp[-g\mu_B H/k_B T]$. This rapid exponential field dependence is absent in Fig. 1. Moreover, numerical calculations predict that $T_{\|}^{-1}$ is negligible in our experiments. Thus, the observed rates are determined entirely by transverse fluctuations, $T_2^{-1} = \eta T_{\perp}^{-1}$, and according to perturbation theory,

$$T_{\perp}^{-1} = (2\pi/\hbar) k_B T \rho^2 \sum_{i,f} |\mathcal{K}_{if}^{(2)}|^2 \delta(E_i - E_f), \tag{6}$$

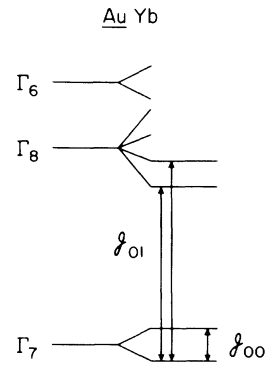

FIG. 2. Zeeman splitting of Yb^{3+} crystal-field levels in Au. The virtual transitions producing nuclear relaxation are indicated for $\vec{H}\|[100]$. For the anisotropic exchange interaction, $\mathcal{J}_{00}$ can be different from $\mathcal{J}_{01}$.

where $\mathcal{K}_{if}^{(2)}$ is the second-order matrix element

$$\mathcal{K}_{if}^{(2)} = \sum_m \frac{\langle f|\mathcal{K}_{ex} + \mathcal{K}_{hf}|m\rangle\langle m|\mathcal{K}_{ex} + \mathcal{K}_{hf}|i\rangle}{E_i - E_m}, \tag{7}$$

and i and f denote, respectively, initial and final states of the nuclear/local-moment/conduction-electron system. The intermediate states m in (7) correspond to virtual excitations of the local moment by $\mathcal{K}_{ex}$ or $\mathcal{K}_{hf}$. We have diagonalized the electronic (crystal field + Zeeman) Hamiltonian as a function of field strength using numerical methods. The resulting eigenfunctions and eigenvalues permit field-induced admixture effects to be treated exactly in the computation of $\mathcal{K}_{if}^{(2)}$. For $\vec{H}_{\|}[100]$, we are restricted by $\mathcal{K}_{hf}$ to transitions to the higher-lying Γ_7 level and two of the Γ_8 levels, as indicated in Fig. 2. Coupling to Γ_6 is nonzero only because of admixture; by taking $\Delta(\Gamma_6$-$\Gamma_7) = 90$ K, the results are essentially independent of Γ_6.

With the isotropic exchange Hamiltonian (1), all three intermediate local-moment states in (7) can be reached for a given set of initial and final conduction-electron states. Contributions to T_2^{-1} from the Γ_7-Γ_7 and Γ_7-Γ_8 virtual transitions therefore add coherently. Using the crystal-field splitting and hyperfine constant obtained in our earlier NMR frequency analysis[9] and $\langle(\mathcal{J}\rho)^2\rangle = 0.016$ from the ESR thermal broadening,[7] we calculate the dashed line in Fig. 1. The theoretical curve agrees well with experiment at 65 kOe but overestimates the relaxation rate at higher fields where $g\mu_B H$ approaches $\sim 0.3\Delta(\Gamma_8$-$\Gamma_7)$ and virtual transitions to Γ_8 consequently become important.

It is illuminating to compute T_2^{-1} due to the Γ_7-Γ_7 transition alone. This produces a theoretical

curve almost identical to the upper solid curve in Fig. 1, which fits the data well even at ~120 kOe. This curve closely obeys a $T_2 \propto H^2$ relationship as expected from a simple model for virtual fluctuations within Γ_7 neglecting admixture corrections. (The simple approach works well because the field-induced admixture affects both states in Γ_7 equally to order H^2.)

In contrast to the isotropic Hamiltonian, the anisotropic Hamiltonian permits at most a single intermediate local-moment state to be reached for a given set of initial and final conduction-electron partial-wave states. According to (2) the angular-momentum index M is exchanged between local-moment and conduction electrons in the exchange scattering. Hence, the conduction-electron processes $kM \rightarrow k'M'$ and $kM' \rightarrow k'M$ permit only the local-moment transition $M \rightarrow M'$, where $|M\rangle$ is the ground state. Consequently, contributions to T_2^{-1} from different intermediate states add incoherently. We ignore corrections to $\mathcal{J}_{MM'}$ due to the field dependence of the energy denominators in (3), and use a constant $\mathcal{J}_{00}$ for exchange within Γ_7 and a constant $\mathcal{J}_{01}$ for Γ_7-Γ_8 exchange.[13] As in the Mössbauer analysis,[4] we adjust ρ^2 by the factor $2/(2J+1) = \frac{1}{4}$ to account for different weights of the $|\vec{k}\sigma\rangle$ and $|kM\rangle$ states. The relaxation times calculated for $(\mathcal{J}_{00}\rho)^2 = 0.0035$ are shown as solid lines in Fig. 1 for three values of the ratio $R_{\mathcal{J}} \equiv \mathcal{J}_{01}/\mathcal{J}_{00}$. A comparison of the results for $R_{\mathcal{J}} \approx 1$ with the isotropic-model prediction demonstrates the large reduction in the Γ_7-Γ_8 contributions resulting from the loss of coherence. The $R_{\mathcal{J}} = 1.5$ case corresponding to the Mössbauer result falls outside the error limits of our experiment unless $(\mathcal{J}_{00}\rho)^2$ is approximately 15% smaller than the Mössbauer value assumed in our calculations. Unfortunately, Gonzalez-Jimenez, Cornut, and Coqblin[4] did not give the uncertainty in their experimental fit. We note in this connection that the Mössbauer linewidth analysis was constrained by (3) which assumes V_{kf} to be independent of M. A relaxation of this constraint would presumably increase greatly the experimental uncertainty in $R_{\mathcal{J}}$. It is possible, in principle, to have $|\mathcal{J}_{01}| < |\mathcal{J}_{00}|$ even though $|E(\Gamma_8)| < |E(\Gamma_7)|$, provided $V_{kf}(\Gamma_8)$ is sufficiently smaller than $V_{kf}(\Gamma_7)$.

We emphasize again that the possibility of significant Γ_8 contributions to $T_\perp^{-1}$ at low temperatures ($k_B T \ll \Delta$) arises from the fact that the nuclear relaxation in this regime is driven by virtual transitions of the local moment. This sensitivity does not apply to the Mössbauer linewidths. These depend on real local-moment transitions which vary as $[\exp(\Delta/k_B T) - 1]^{-1}$ instead of T/Δ^2 and thus become important only at higher temperatures, as actually observed.[4] Finally, we remark that the Kondo anomalies observed in the low-field Mössbauer data are suppressed in fields above ~10 kOe,[13] justifying the neglect of higher-order (i.e., $\ln T$ and $\ln H$) contributions in our analysis.

In conclusion, our experimental results are inconsistent with the isotropic exchange Hamiltonian. Although we cannot determine the value of $R_{\mathcal{J}}$ unequivocally, our results strongly support an anisotropic interaction for Yb^{3+}.

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