$\vec{k}$ Dependence of the Conduction-Electron–Local-Moment Exchange Interaction in the Atomic and Covalent-Mixing Limits

D. H. Lowndes,[a] C. Lin Hendel,[b] and R. Hendel[b]
University of Oregon, Eugene, Oregon 97403

and

G. W. Crabtree
Argonne National Laboratory, Argonne, Illinois 60439
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The $\vec{k}$ dependence of the conduction-electron–rare-earth-moment exchange interaction is directly measured for the first time and found to be opposite in sense for Gd and Yb impurities in Au. Atomic exchange dominates for Au(Gd), while a phase-shift analysis indicates that covalent mixing of conduction *p waves* accounts for the observed $\vec{k}$ dependence in Au(Yb).

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The nature of the conduction-electron–local-moment exchange interaction in metals is a fundamental problem which has stimulated widespread interest. It is known empirically[1] that the exchange integral J which is observed in metals is the sum of two contributions with distinctly different origins: $J = J_{at} + J_{cm}$. J_{at} is the atomic ("direct" or "on-site") contribution,[2-4] which would occur also in a nonmetallic host containing magnetic impurities. If the conduction states $\psi_{\vec{k}}$ and the local states φ_l are known, J_{at} can be calculated by evaluating the exchange integral

$$J(\vec{k},\vec{k}') \propto \sum_l \int \psi_{\vec{k}}^*(\vec{r}_1)\varphi_l^*(\vec{r}_2)|\vec{r}_1 - \vec{r}_2|^{-1} \times \psi_{\vec{k}'}(\vec{r}_2)\varphi_l(\vec{r}_1)\, d^3r_1\, d^3r_2$$

in a straigntforward way. Such integrals are inherently ferromagnetic in sign $[J(\vec{k},\vec{k}')>0]$. J_{cm} is the covalent-mixing contribution[3-7] which is attributed to spin polarization of the conduction electrons in the neighborhood of a magnetic impurity. It arises from hybridization of the local magnetic states with the conduction-electron states, creating net conduction-electron spin opposite to that of the impurity. This is equivalent to an antiferromagnetic exchange coupling and leads to spin compensation of the local moment and a variety of Kondo anomalies in various properties.

Theoretical models for both the atomic and covalent-mixing contributions are usually simplified by assumption of a single exchange constant for coupling between all conduction-electron states and the impurity. In this paper we present direct experimental evidence for significant $\vec{k}$ dependence of the exchange coupling in both the atomic and covalent mixing limits. We find that the strength of the interaction varies in opposite directions for the two cases, and in the covalent-mixing case correlates with the p character of the conduction states. We also report the first measurements of the $\vec{k}$ dependence of the up- and down-spin scattering rates for conduction electrons from rare-earth impurities and show how these data can be interpreted by the $5d$ virtual-bound-state model.

As prototypes of atomic and covalent mixing exchange we have chosen dilute alloys of Au(Gd) and Au(Yb), respectively. Gd has a very stable moment in all metallic hosts and always displays atomiclike ferromagnetic coupling.[8-10] Conversely, Yb is strongly affected by hybridization as evidenced by its variable valence (trivalent in Au but divalent in Ag)[11] and net antiferromagnetic exchange coupling, leading to Kondo anomalies at $T_K \sim 0.01$ K.[12] Such clear examples of atomic and covalent-mixing exchange are impossible to find among transition-metal solutes in noble-metal hosts.

Our results were obtained from an analysis of the amplitude, harmonic content, and spin-splitting zeros of de Haas–van Alphen (dHvA) oscillations in fields between 1.5 and 8.0 T and temperatures between 1 and 4.2 K. Single crystals containing 295 at. ppm Gd and 260 and 180 at. ppm Yb were grown by the Bridgman method in a vacuum of 2×10^{-5} Torr. The samples were spark cut to size ($1\times1\times3$ mm^3), etched in aqua regia, and annealed for up to 50 h at 850°C in a vacuum of 2×10^{-7} Torr. Measurements of the orbital exchange splitting ΔE_x of opposite-spin Landau levels were performed on neck orbits for $\hat{H}$ along ⟨111⟩ using wave-shape analysis and at the spin-splitting zeros of the second dHvA harmonic which occur 14–21° away from ⟨111⟩ depending on field strength and impurity content. Severe magnetic interaction and the absence of spin-splitting zeros prevented measurements of ΔE_x on the belly region of the Fermi surface. A complete set of orbital scattering-rate measurements was carried out for the ⟨100⟩ and ⟨111⟩ belly, ⟨100⟩ rosette, ⟨110⟩ dogsbone, and ⟨111⟩ neck orbits from measurements of the dHvA fundamental amplitude. The wave-shape analysis,[13] spin-splitting zero,[14,15] and scattering-rate measurement techniques[16] are fully described elsewhere.

For neither alloy [nor for Au(Ho), to be reported elsewhere[17]] was any significant spin-dependent scattering observed. This is a somewhat surprising result, in view of the well-defined local moment on the impurity site. The measured spin-independent scattering rates for the various orbits are shown in Fig. 1, together with theoretically predicted scattering-rate anisotropies for p- and d-wave scattering of the conduction-electron states. For both Gd and Yb, the observed scattering-rate anisotropy lies entirely within the range expected for pure d-wave scattering, and very near the average for states belonging to both irreducible representations.

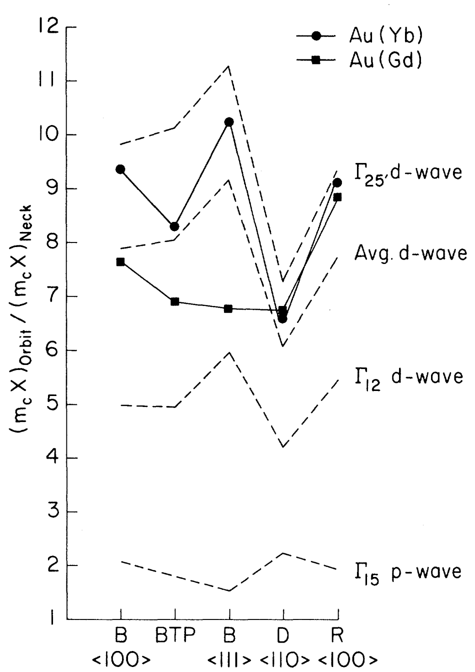

FIG. 1. Comparison of the measured orbital Dingle temperature ratios, $(m_cX)_{\rm orbit}/(m_cX)_{\rm neck}$, with the theoretically calculated orbital scattering anisotropy factor $(W_{ll}{}^{\Gamma})_{\rm orbit}/(W_{ll}{}^{\Gamma})_{\rm neck}$, for scattering of pure l waves belonging to cubic group irreducible representation Γ (dashed lines, from Ref. 17). m_c is the orbital cyclotron effective mass. The extremal orbits are the ⟨100⟩ belly, the belly turning point, the ⟨111⟩ belly, the ⟨110⟩ dogsbone, and the ⟨100⟩ rosette, all with $\hat{H}$ in the (110) plane.

We interpret the spin-independent d-wave resonant scattering observed for both alloys in terms of the $5d$ virtual-bound-state model for rare-earth impurities in noble-metal hosts, which has been used to explain the large crystal-field splitting[18] and excess resistivities[19] found in these systems. The model assumes a partially occupied local $5d$-like virtual state around the impurity site which is sufficiently broadened by hybridization with conduction states that it is nonmagnetic. The scattering from such a nonmagnetic $5d$-like state should exhibit two defining characteristics: a strong d resonance, and an absence of spin-dependent effects, exactly as we observe. The absence of spin-dependent scattering for rare-earth impurities is in sharp contrast with first-row transition-metal impurities in Au, which typically show strong spin-dependent scattering.[16] In that case, the local $3d$ state responsible for the scattering also contains the magnetic electrons, so that the scattering process is inherently spin dependent.

Table I shows the results for measurements of the exchange interaction by both wave-shape analysis and spin-splitting zero techniques for neck orbits. As for the pure-Au spin-splitting zeros,[15] only one choice of argument for the cosine factor makes physical sense, and so the question of 2π ambiguity does not arise. We define an exchange constant $J_{\rm orb}$ for each orbit by $2\Delta E_x = J_{\rm orb}\, c^*\langle S_z\rangle$, where $2\Delta E_x$ is the splitting of opposite-spin conduction levels due to exchange interactions,[13,14] c^* is the impurity concentration, and $\langle S_z\rangle$ is the expected value of the impurity spin, assumed to be saturated by the high fields used in these experiments ($\langle S_z\rangle = \frac{7}{2}$ for Gd and $\frac{1}{2}$ for Yb). With this definition, $J_{\rm orb}$ is the average value of the diagonal term $J(\vec{k},\vec{k})$ around a cyclotron orbit.

For Au(Gd) we observe exchange coupling which is *ferro*magnetic in sign, with significant anisotropy of $J_{\rm orb}$: $J_{\rm orb}$ is a maximum at ⟨111⟩ and *decreases* by approximately 20% for only a 14° change in field direction, away from ⟨111⟩.

For Au(Yb) the sign, the magnitude, and the sense of the anisotropy of $J_{\rm orb}$ are all different: *anti*ferromagnetic exchange coupling approximately an order of magnitude stronger than for Au(Gd),

TABLE I. Summary of measured exchange couplings between rare-earth impurities and conduction electrons for various neck orbits in Au.

Alloy	Concentration (at. ppm)	θ (deg)[a]	H (kG)	T (K)	Method[b]	J_{orb}
Au(Gd)	295	54.7		1.08	WA	$+0.076 \pm 0.006$
		40.4	69.3	1.1	SSZ	$+0.060 \pm 0.006$
Au(Yb)	260	54.7		1.1	WA	-0.60 ± 0.04
		74.7	75.1	1.1	SSZ	-0.78 ± 0.09
		75.5	64.8	1.1	SSZ	-0.92 ± 0.07
Au(Yb)	180	54.7		1.34	WA	-0.48 ± 0.06

[a] Angle in degrees from ⟨100⟩ in the (110) plane. ($\theta = 54.7°$ is the ⟨111⟩ direction).

[b] SSZ is the second-harmonic spin-splitting zero; WA is wave-shape analysis using three dHvA harmonics. Each WA result is the average derived from separate harmonic analysis of approximately ten data blocks over the field range $43 \leq H(\text{kOe}) \leq 75$.

and *increasing* more than 50% in strength as the magnetic field is tipped 20° away from ⟨111⟩.

The overall magnitudes and signs of J_{orb} we observe are in good agreement with Fermi-surface–averaged J values derived from measurements of local moment properties: $J = +0.1$ eV for Au(Gd) from EPR,[10] and for Au(Yb) $J = -0.85$, -0.55, and -0.51 eV from EPR,[1] Mössbauer,[20] and resistivity[21] measurements, respectively. [The resistivity results have been corrected by a factor $(2l+1)^{2/3}$ where $l = 3$ for rare-earth systems.[4]]

For Au(Gd) the small magnitude of J_{orb} suggests a near cancellation of the atomic and covalent contributions. For comparison, Tao *et al.*[1] used EPR measurements in Au(Er) to estimate $J_{at} \sim 0.15$ eV, $J_{cm} \sim -0.05$ eV, and $J \sim 0.10$ eV, very similar to the magnitude we observe in Au(Gd). The decrease in J_{orb} as the neck orbit is tilted off ⟨111⟩ is then predominantly a measure of anisotropy of the atomic contribution, partially masked by the covalent-mixing contribution discussed below. Because the atomic and covalent-mixing contributions are apparently the same order of magnitude in Au(Gd), a complete analysis of the anisotropy requires more detailed theoretical guidance and is not warranted at this time.

For Au(Yb), the large magnitude and negative sign of J_{orb} indicate that covalent mixing is overwhelmingly dominant, so that the increase in magnitude as the field is tipped off ⟨111⟩ is characteristic of J_{cm}. Assuming that the covalent-mixing exchange occurs via hybridization of the f states with a single conduction electron l wave, $J_{cm}(\vec{k},\vec{k})$ would scale with both the local l-wave charge density and the local density of states (i.e., the inverse Fermi velocity) at $\vec{k}$. The quantity scaling with J_{orb} would then be $\partial A/\partial \eta_l$, the orbital weighting factor occurring naturally in the phase-shift parametrization of various Fermi-surface properties.[22] Subtracting $J_{at} \sim +0.15$ eV from the measured values of J_{orb} for Au(260-ppm Yb) in Table I gives J_{cm} in the ratio 1:1.24(± 0.25): 1.43(± 0.2) (increasing away from ⟨111⟩). The corresponding p-wave (d-wave) orbital weighting factors stand in the ratio 1:1.28:1.32 (1:1.68:1.78).[23] The observed anisotropy of J_{cm} is thus consistent in both magnitude and sense with exchange via the conduction-electron p waves, i.e., a p-f covalent-mixing exchange interaction. If the Fermi-surface average of J_{orb} is estimated with the assumption of p-wave scaling, we find $J_{FS} \sim -1.0$ eV, in good agreement with other measurements. In contrast, scaling by d waves yields $|J_{FS}| > 4$ eV.

In summary, the scattering data for both Au(Gd) and Au(Yb) show the existence of a nonmagnetic d resonance, a direct confirmation of the most basic features of the 5d virtual-bound-state model. The significant $\vec{k}$ dependence of the exchange coupling which we find for both the atomic and covalent-mixing limits shows that the widely used models assuming a single exchange coupling for all conduction and impurity states do not adequately describe the exchange interaction in dilute alloys. When this is considered with the work of Follstaedt and Narath,[24,25] who showed experimentally that the magnetic and crystal-field–split sublevels of Yb impurities in Au hosts couple to the conduction electrons with different strengths, one appreciates the considerable distance still separating theory and experiment even for these relatively simple cases. We suggest that the Au(Yb) system, which displays clear covalent-mixing character and has a relatively simple electronic structure, and for which there is now an extensive body of experimental data, is an excellent candidate for further theoretical work.

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[(a)]Present address: Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

[(b)]Present address: Tektronix, P.O. Box 500, Beaverton, Ore. 97077.

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Planar Coupling Mechanism Explaining Anomalous Magnetic Structures in Cerium and Actinide Intermetallics

Robert Siemann and Bernard R. Cooper
Department of Physics, West Virginia University, Morgantown, West Virginia 26506
(Received 4 December 1979)

Cerium and light actinide monopnictides of NaCl structure have extraordinarily strong magnetic anisotropy, with unusual magnetic structures and transitions. We show that this behavior can be understood on the basis of a Coqblin-Schrieffer–type interaction, effectively treating mixing of f and conduction electrons.

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Cerium and light actinide monopnictides of NaCl structure show remarkably anisotropic magnetic properties[1] favoring $\langle 100\rangle$ alignment, and exhibiting transitions between unusual linear magnetic structures. An important feature[2] is the extreme anisotropy of the moment correlations in USb, showing stronger interactions within ferromagnetic sheets than between them.

The peculiar magnetic structural behavior and transitions cannot be explained by the previously

