Knight Shift Anomalies in Heavy Electron Materials

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We calculate nonlinear Knight shift K vs susceptibility χ anomalies for Ce ions possessing local moments in metals. The ions are modeled with the Anderson Hamiltonian and studied within the noncrossing approximation. The K vs χ nonlinearity diminishes with decreasing Kondo temperature T_0 and nuclear-spin–local-moment separation. Treating the Ce ions as an incoherent array in $CeSn_3$, we find excellent agreement with the observed Sn $K(T)$ data.

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The origin of Knight shift anomalies in metals with localized moments that undergo the Kondo effect has been a subject of great interest in the condensed matter community over a period of nearly 25 years [1–11]. The central physical concept is that the many body screening cloud surrounding a Kondo impurity site should give rise to an anomalous temperature dependent Knight shift at nuclear sites due to the coupling of the local moment to the nuclear spin through the screening cloud [1,3–5,9,10]. This would be manifest in a deviation from a linear relation of the Knight shift K to the magnetic susceptibility χ below the Kondo temperature T_0 (such a "nonlinear Knight shift anomaly" is to be distinguished from the nonlinear susceptibility related to the field dependence of χ). Another way to say this is that in the absence of an anomaly the contribution $K(\vec{r},T)$ from a local moment at distance $\vec{r}$ from the nucleus can be written as $f(\vec{r})\chi(T)$. This factorization does not hold if there is an anomaly [instead $K(\vec{r},T) = f(\vec{r},T)\chi(T)$ due to the temperature dependent polarization cloud]. The classic experiments by Boyce and Slichter [2] on the low Kondo temperature ($T_0 \simeq 10$ K) alloy Fe:Cu displayed no evidence for this anomalous Knight shift behavior. In contrast, pronounced Knight shift anomalies have been observed in the concentrated heavy electron materials $CeSn_3$ [6,8] and YbCuAl [7,8], which have been described as Kondo lattice systems with $T_0 \simeq 400$ K. In view of the Boyce-Slichter result, the question is raised whether these anomalies represent a coherent effect of the periodic lattice rather than a single ion effect. However, recent experiments on the proposed quadrupolar Kondo alloy [12,13] $Y_{1-x}U_xPd_3$ demonstrate that for concentrations of 0.1–0.2 there are pronounced nonlinearities in the Y Knight shift for sufficiently large distances away from the U ion [11].

In this Letter, we present some results from our systematic theoretical studies of the Knight shift in heavy electron materials. We find, as expected from earlier analytic theories, that the magnitude of the Knight shift anomaly is reduced with decreasing Kondo temperature and decreasing distance between local moment and impurity sites. Ours is the first study to display this effect in a realistic model calculation for Ce ions with an oversimplified conduction band structure. We find that the Knight shift anomaly of $CeSn_3$ can be plausibly accounted for by incoherent, single ion physics. In particular, by carrying out a full lattice sum on $CeSn_3$, we obtain an excellent one parameter fit of the calculated Knight shift to the experimental one, in spite of the oversimplified treatment of conduction electrons in our model calculation.

The application of NMR in Kondo systems received impetus from Heeger [1] who suggested that the anomalous cloud was detectable in Knight shift measurements. Essentially, the oscillatory conduction spin density $\vec{s}(\vec{r})$ induces a local-moment–nuclear-moment interaction. In the limit $T_0 \longrightarrow 0$, this interaction $I(\vec{r})$ is well described by the second order perturbation theory Ruderman-Kittel-Kasuya-Yosida expression $[\vec{s}(r) \sim I(\vec{r}) \sim \cos(2k_F r)/r^3]$. Ishii [4,5] confirmed that for an $S_I = \frac{1}{2}$ pure-spin Kondo impurity (with no charge fluctuations) an anomalous conduction spin density cloud sets in beyond the Kondo screening length $\xi_K = \hbar v_F / k_B T_0$, where v_F is the Fermi velocity. Inside this radius, conventional temperature independent RKKY oscillations dominate of the kind observed by Boyce and Slichter [2]. Outside the screening length, at $T = 0$, the anomalous term will dominate also with an RKKY form but an amplitude of order D, the conduction bandwidth, compared with $D(N(0)J)^2$ for the Ruderman-Kittel term, where $N(0)$ is the conduction-electron density of states at the Fermi energy and J the conduction-electron–local-moment exchange coupling. Ishii did not calculate the explicit temperature dependence of this structure, but did anticipate that it would vanish above the Kondo scale. Scaling analysis confirmed the asymptotic factorization of the Knight shift for short distance and low temperature [9]. A possible understanding of the Boyce and Slichter results, then, is that the Cu nuclei they sampled were at distances $r \ll \xi_K$ from the Fe ions.

In an Anderson model treatment of the problem, charge fluctuations are allowed. Consider, for example, a Ce ion with nominally one f electron giving rise to the local

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moment. The ensuing Kondo effect is best understood in terms of a mixing of the empty configuration with one in which the Ce moment is screened by a superposition of conduction hole states. This opens up new possibilities for detecting the anomalous screening cloud. One interpretation of the Boyce-Slichter results is that due to subtleties of spin conservation in the singlet ground state the spin cloud is unobservable, while the anomalous charge cloud is observable through electronic field gradient measurements at atomic nuclei [3].

We shall focus on the second possibility, that the anomalous spin cloud now has a finite amplitude within $r < \xi_K$ which is proportional to the weight of f^0 in the ground state. This anomaly scales approximately linearly with T_0, so the cloud will be virtually undetectable in small T_0 systems, but may be observable in high T_0 systems. Our results support this picture as we shall explain in more detail.

Our starting point is an Anderson model Hamiltonian. We shall first discuss the situation for Ce^{3+} and Yb^{3+} ions, and write down the model only for the Ce case. For a single Ce site at the origin, the model is

$$\mathcal{H} = \mathcal{H}_c + \mathcal{H}_f + \mathcal{H}_{cf} + \mathcal{H}_z \tag{1}$$

with

$$\mathcal{H}_c = \sum_{\vec{k}\sigma} \epsilon_k c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} \tag{2}$$

the conduction band term for electrons with a broad featureless density of states of width D, taken to be Lorentzian here for convenience; with

$$\mathcal{H}_f = \sum_{jm} \epsilon_{fj} |f^1 jm\rangle\langle f^1 jm| \tag{3}$$

where $j = \frac{5}{2}, \frac{7}{2}$ indexes the angular momentum multiplets of the Ce ion having azimuthal quantum numbers m, with $\epsilon_{f5/2} = -2$ eV, $\epsilon_{f7/2} = \epsilon_{f5/2} + \Delta_{\text{so}} = -1.7$ eV (we take the f^0 configuration at zero energy); with

$$\mathcal{H}_{cf} = \sum_{\vec{k}jm\sigma} [V_{\vec{k}j\sigma m} c^{\dagger}_{\vec{k}\sigma} |f^0\rangle\langle f^1 jm| + \text{H.c.}] \tag{4}$$

where $V_{\vec{k}j\sigma m} = VY_{3m-\sigma}(\hat{k})\langle 3m - \sigma, 1/2\sigma | jm\rangle/\sqrt{N_s}$, V being the one particle hybridization strength and N_s the number of sites; and with

$$\mathcal{H}_z = -\mu_B H_z \left[2\sum_{\vec{k}\sigma} \sigma n_{\vec{k},\sigma} - \sum_{jm} g_j m |f^1 jm\rangle\langle f^1 jm| \right] \tag{5}$$

being the Zeeman energy of the electronic system for a magnetic field H_z applied along the z axis. In addition to this, we must add a term coupling the nuclear-spin system to the conduction electrons, which we take to be of a simple contact form $\sim \vec{I}(\vec{r}) \cdot \vec{S}(\vec{r}_I)$ for each nuclear spin $\vec{I}(\vec{r})$ at position $\vec{r}$ with $\vec{S}(\vec{R})$ the conduction spin density at the nuclear site, and a nuclear Zeeman term. In terms of the parameters, the Kondo scale characterizing the low energy physics is given by

$$k_B T_0 = D\left(\frac{D}{\Delta_{\text{so}}}\right)^{4/3} \left(\frac{\Gamma}{\pi|\epsilon_{f5/2}|}\right)^{1/6} \exp\left(\frac{\pi \epsilon_{f5/2}}{6\Gamma}\right) \tag{6}$$

where the hybridization width $\Gamma = \pi N(0) V^2$.

We treat the Anderson Hamiltonian with the noncrossing approximation (NCA), a self-consistent diagrammatic perturbation theory discussed at length in the paper of Bickers, Cox, and Wilkins [14]. This approximation is controlled by the large orbital degeneracy of the Ce ground state. It does show pathological behavior (due to the truncation of the diagrammatic expansion) for a temperature scale $T_p \ll T_0$ in this conventional Anderson model, provided the f^1 occupancy $n_f \geq 0.7$. In practice, this is not a problem for $N \geq 4$ as shown in Ref. [14], in that comparison of NCA results with exact thermodynamics from the Bethe ansatz shows agreement at the few percent level above T_p. Hence this is a reliable method for our purposes.

The approach in the NCA is to write a propagator for each ionic state of the Ce site (i.e., $f^1 j = \frac{5}{2}, \frac{7}{2}$ and f^0 in the present model), solve self-consistent integral equations to second order in the hybridization for the ionic propagator self-energies, and then calculate physical properties as convolutions of these propagators. To evaluate the Knight shift we employ the lowest order diagram coupling nuclear spin to Ce magnetic moment, as shown in Fig. 1. The full expression corresponding to this diagram is cumbersome and will be presented in detail elsewhere. To the extent that the dynamics of the empty orbital can be neglected, this expression factorizes into a nearly temperature independent RKKY interaction (modified due to the spin-orbit coupling and anisotropic hybridization from the original form) times the f-electron susceptibility. Thus, no anomaly results from the diagram in this limit. In this limit, the susceptibility in the diagram corresponds to the leading order estimate used in Ref. [14] to compare with exact Bethe ansatz results.

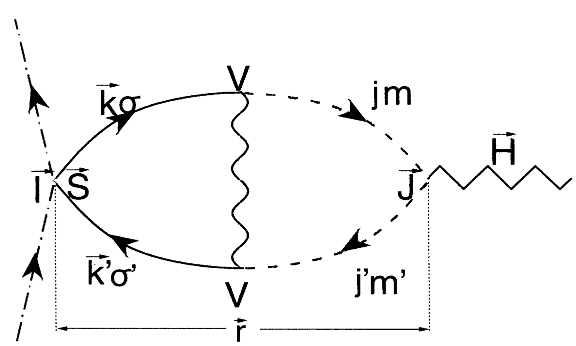

FIG. 1. Feynman diagram of coupling between Ce local moment and nuclear spin in the infinite U Anderson model. The dashed line represents the singly occupied (f^1) state and the wavy line the empty orbital (f^0) state. The solid line represents the conduction electron. The dot-dashed line is a propagator for the nuclear-spin states and $\vec{H}$ is the external magnetic field.

However, for $T = 0$, the empty orbital propagator may be written in an approximate two-pole form, one with amplitude $1 - Z$, $Z = \pi k_B T_0/6\Gamma$, centered near zero energy, and one with amplitude Z centered at $\sim\epsilon_{f5/2} - k_B T_0$ which reflects the anomalous ground state mixing due to the Kondo effect. The first term gives conventional RKKY oscillations modulo the anisotropy and altered range dependence induced by the $m, \hat{k}$ dependence of the hybridization. The amplitude of the second term goes to zero above the Kondo temperature. It is this term which may be traced to the anticipated anomalous Knight shift, and within such a two-pole approximation may be seen to be finite within ξ_K, have a stronger distance dependence in that regime, but possess an amplitude of order Z only within this distance regime. Beyond ξ_K, the amplitude is of order $1/N$ and the shape of the spin oscillations is the same as that found from the high frequency pole of the empty orbital propagator.

The diagram of Fig. 1 has been studied with the NCA previously [10], but only for the spin $\frac{1}{2}$ model with infinite Coulomb repulsion, and for a limited parameter regime (very low T_0 values) and short distances ($r \ll \xi_K$). Consequently, no strong evidence was found for a Knight shift anomaly in this previous work.

Our numerical procedure, briefly, consists of solving the NCA integral for the Anderson Hamiltonian specified above on a logarithmic mesh with order 600 points chosen to be centered about the singular structures near the ground state energy $E_0 \sim \epsilon_{f5/2}$. We then feed the self-consistent propagators for the empty and singly occupied orbitals into the convolution integrals obtained from the diagram of Fig. 1, which allows for evaluation of the Knight shift at arbitrary angle and distance from the nuclear site. It is convenient to take the nuclear site as the origin in this case leading to phase factors $e^{-i\vec{k}\cdot\vec{r}}$ in the hybridization Hamiltonian $\mathcal{H}_{cf}$, where $\vec{r}$ is the nuclear-Ce site separation. These factors give the oscillations and position space angular dependence in K. All contributions from the Ce susceptibility are included.

To demonstrate the dependence of the K vs χ anomaly as a function of Kondo scale T_0, we have evaluated the diagram of Fig. 1 for a single local moment placed at a fixed distance $r = 3.3k_F^{-1} = 3.3$ Å for our choice of $k_F = 1$ Å^{-1} and angle of 0° with respect to the quantization axis. We have tuned the Kondo scale by holding fixed all parameters except the hybridization. The Knight shift is scaled to a susceptibility by matching at high temperatures, and the susceptibility units are scaled by a fit of one calculation to the data for $CeSn_3$ assuming $D = 3$ eV. The results are shown in Fig. 2(a). Clearly, as the Kondo scale is reduced, the magnitude of the deviation from a linear K vs χ relation is systematically reduced. Also, as the separation r is decreased [cf. Fig. 2(b)] the magnitude of the K vs χ nonlinearity diminishes. Very similar results are obtained for Yb compounds (theYb^{3+} ion has a lone $4f$ hole and our procedure describes these with a simple

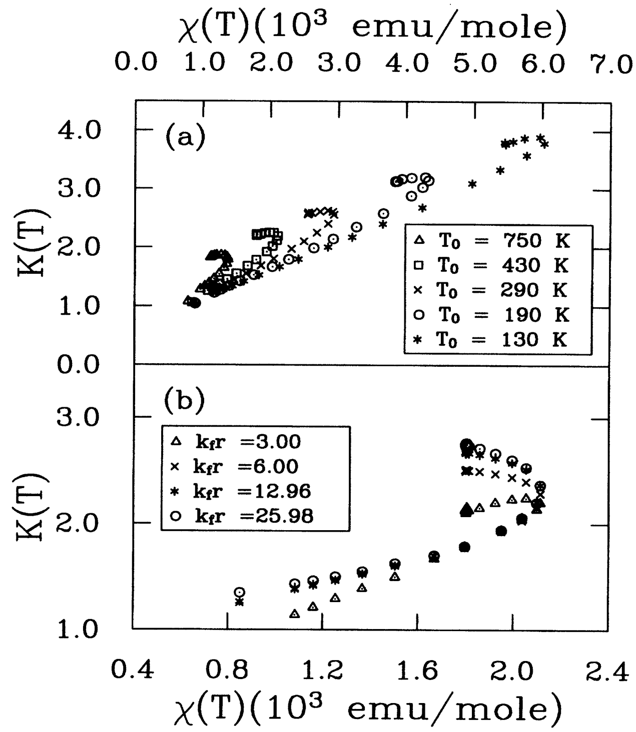

FIG. 2. (a) Calculated Knight shift $K(T)$ vs susceptibility $\chi(T)$ for a single Ce site at $k_F r = 3.33$ from a nuclear moment and angle $\Theta = 0$. Fixing the f-level energy $\epsilon_{5/2} = -2$ eV and the spin-orbit splitting $\Delta_{so} = 0.3$ eV, the hybridization is varied to illustrate the dependence of the nonlinearity on the magnitude of T_0 (which ranges from 750 to 130 K in these calculations as Γ varies from 0.165 to 0.130 eV, which sets the scale of Z variation—see text). The diagram of Fig. 1 is used to calculate $K(T)$. The magnitude of the nonlinearity diminishes as T_0 is reduced. The theoretical Knight shift has been shifted by a common offset and scale factor to match the susceptibility. (b) Calculated Knight shift $K(T)$ for a single Ce site vs susceptibility $\chi(T)$ for varying separation with the Kondo scale used to fit the $CeSn_3$ $\chi(T)$ (see Fig. 3). For each plot the angle is held at θ with respect to the nuclear moment–Ce axis. The magnitude of the nonlinearity diminishes as $k_F r$ is reduced. The theoretical Knight shifts have been shifted by offset and scale factors to match the susceptibilities; this does not affect the relative size of the anomaly.

particle hole transformation, which we will discuss in detail in a subsequent publication).

To assess the relevance of this single site physics to the periodic compound $CeSn_3$ we have performed a lattice sum about a given Sn nucleus from all surrounding Ce ions. We assume the Knight shift contribution of each ion to be described by this single site physics, known to be a good approximation at high temperatures where the ions are incoherent with one another, and known to provide a very accurate description of the thermodynamics in many cases. We carried out the sum to several hundred shells about the Sn site, obtaining good convergence at all calculated temperatures. We fixed the parameters by fitting the susceptibility data of $CeSn_3$. The result is shown in Fig. 3, where we have scaled the Knight shift by an intermediate range temperature match to the susceptibility (note that the NMR data of Ref. [6] extend only to room temperature). Clearly the agreement between theory and experiment is impressive [15]. There are several notable features here: (i) the calculated amplitude of our Knight shift prior to scaling is actually negative, which implies that the fit is sensible only if the assumed contact coupling between conduction and nuclear spins is negative, which actually makes sense because the Sn nucleus should predominantly couple through core polarization; (ii) the magnitude of the anomaly goes in the right direction and begins at the right temperature to agree with the experimental anomaly [6], despite the highly oversimplified conduction band we are employing; (iii) the magnitude of the anomalous contribution from the Ce sites does go down with distance from the Sn nucleus—the theoretical data which most closely match those of experiment are taken at the fixed distance $r = 3k_F^{-1} = 3$ Å and angle of 0°. However, the anomaly is then still surprisingly large even at this short distance.

We cannot accept uncritically the excellent agreement of our calculation with experiment due to (a) our oversimplified band structure and (b) the neglect of lattice coherence effects. We note that in the lattice the repeated scattering of conduction electrons off the Ce ions (now in every unit cell) may have the effect of reducing the screening length [16]. We intend to study this within a local approximation ($d = \infty$ expansion) to the lattice model. A calculation of the ^{27}Al Knight shift in YbCuAl with the same method and lattice sum procedure gives the correct magnitude for the anomaly but the wrong sign. We are unsure whether this is due to our simple band structure or coherence effects. In either case ($CeSn_3$ or YbCuAl), we believe that the single site Kondo effect can clearly explain the magnitude of the observed Knight shift anomaly and thus serves as an important point of comparison for future theoretical work in this area.

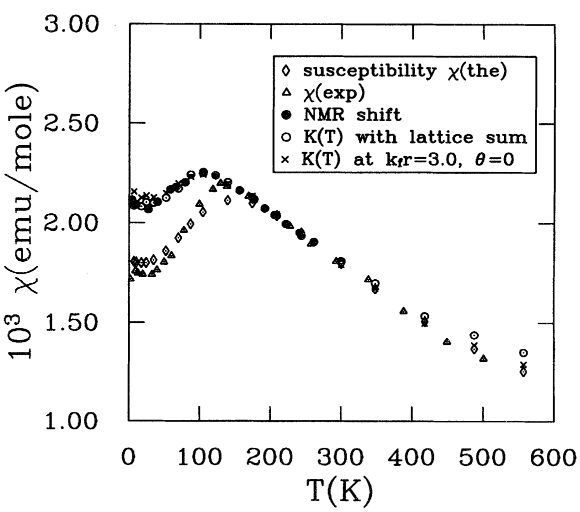

FIG. 3. Temperature dependence of Sn Knight shift $K(T)$ and Ce $\chi(T)$ (both calculated and experimental results [6]) for $CeSn_3$. The theoretical $K(T)$ is calculated using the diagram of Fig. 1 and with T_0 chosen to fit the experimental $\chi(T)$ data. A full (incoherent) lattice sum is carried out over several hundred shells of atoms.

In summary, we have computed Knight shift anomalies within a realistic model for Ce ions in metals for the first time. We find that the magnitude of the nonlinearity scales down in size as the Kondo scale is diminished or the nuclear-moment–local-moment separation is reduced. Modeling the Ce ions incoherently in $CeSn_3$, we find that summing over all lattice sites the resulting Sn Knight shift agrees quite well with experiment, while for the Al Knight shift in YbCuAl a corresponding calculation gives well the magnitude of the anomaly, though not the sign. Future work needs to utilize more realistic band structures and examine the effects of the lattice coherence among conduction states.

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