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Anomalous NMR magnetic shifts in $CeCoIn_5$

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We report ^{115}In and ^{59}Co nuclear magnetic resonance (NMR) measurements in the heavy fermion superconductor $CeCoIn_5$ above and below T_c. The hyperfine couplings of the ^{115}In and ^{59}Co are anisotropic and exhibit dramatic changes below 50 K due to changes in the crystal field level populations of the Ce ions, suggesting localized f electrons. Below T_c the spin susceptibility is suppressed, indicating singlet pairing.

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In heavy fermion systems the interplay of magnetism and superconductivity gives rise to a diverse range of ground states including an unconventional form of superconductivity. The recently discovered family of heavy fermion compounds CeMIn$_5$, where M=Co, Rh, or Ir exemplifies these effects. Whereas the Rh compound undergoes a transition from antiferromagnetic to superconducting under pressure,[1] the Ir (Ref. 2) and Co (Ref. 3) compounds superconduct at ambient pressure, with the Co system exhibiting the highest known transition temperature (2.3 K) for any heavy fermion system. Evidence from heat capacity and thermal transport indicate that the pairing symmetry in the superconducting state is unconventional and that there are line nodes in the superconducting gap.[4]

The bulk magnetic susceptibility, χ, of tetragonal CeMIn$_5$ displays systematic trends consistent with the diversity of observed ground states. In all three cases χ is anisotropic, and is largest for field applied along the c direction. In the ab plane, χ_{ab} is essentially the same for all three materials. However, χ_c exhibits a maximum at $\sim$10 K for $CeRhIn_5$ (T_N=3.8 K), whereas for the superconductors $CeIrIn_5$ and $CeCoIn_5$ χ_c diverges at low temperatures until T_c is reached. For both of these materials χ_c also exhibits a plateaulike feature around 50 K, which is less pronounced for the Ir system. The origin of this feature and the relationship between χ_c and T_c have been debated; however, both the plateau and the divergence are intrinsic and independent of field.[3]

Here we report a detailed study of site-specific magnetic shifts in $CeCoIn_5$ using nuclear magnetic resonance (NMR). Measurements in the normal state provide a microscopic measure of the local susceptibility and we find anomalous temperature dependencies. This behavior is likely due to the thermal depopulation of a crystal field (CEF) excitation of the Ce ions. We find remarkably strong departures from the expected proportionality between bulk susceptibility and the NMR Knight shift. We argue that this effect is indicative of a high degree of Ce moment localization, a feature that may play a role in the mechanism for superconductivity in this material and puts important constraints on any microscopic theory. In the superconducting state the temperature dependencies of the shifts reveal a suppression of the spin susceptibility consistent with spin-singlet pairing.

Crystals of $CeCoIn_5$ were grown from an In flux as described in Ref. 3. The tetragonal crystal structure of $CeCoIn_5$ consists of alternating layers of $CeIn_3$ and $CoIn_2$ and so has two inequivalent In sites per unit cell. The In(1) site has axial symmetry and is analogous to the single In site in cubic $CeIn_3$. There are four low symmetry In(2) sites per unit cell, two on each of the lateral faces of the unit cell, located a distance 0.306c above and below the Ce-In layer.[5,6] The zero field ^{115}In (I=9/2) nuclear quadrupolar resonance (NQR) spectrum reveals an axially symmetric site with $^{115}\nu_Q$ (1) $=8.173\pm0.005$ MHz, and $\eta(1)=0.0$ at 4 K, whereas the electric field gradient (EFG) at the In(2) site is characterized by $^{115}\nu_Q$ (2)$=15.489\pm0.001$ MHz, and $\eta(2)=0.386 \pm0.001$, where ν_Q and η are defined as in Refs. 7 and 8. The NMR spectrum of the ^{59}Co (I=7/2) indicates a site with axial symmetry and $^{59}\nu_Q=234\pm1$ kHz at 4 K. Both the In and the Co EFG's are essentially temperature independent, varying less than 0.5% between 4 K and 100 K, indicating that significant structural changes are absent in this temperature range.

The magnetic shift measurements were made on a large single crystal of $CeCoIn_5$, which was mounted with the c axis either parallel or perpendicular to the external field, for fields between 3 and 5 T. Field-swept spectra were obtained by measuring the spin echo intensity as a function of applied field at fixed frequency. The shifts were determined by measuring several of the ^{115}In transition fields $H_{\rm exp}$ for each site at several different fixed frequencies. The nuclear spin Hamiltonian $\mathcal{H}=(h\nu_Q/6)[3I_z^2-I^2+\eta(I_x^2-I_y^2)]+\gamma\hbar\mathbf{I}\cdot(\mathbf{1}+\mathbf{K})\cdot\mathbf{H}_0$, where $\mathbf{K}=(K_a,K_b,K_c)$ is the magnetic shift tensor, was diagonalized and the resonance fields $H_{\rm res}$ for each transition and each In site were then calculated. The spectra were then fit by minimizing $\chi^2=\Sigma_i(H_{\rm res}-H_{\rm exp})^2$ as a function of (θ,ϕ,K_a,K_b,K_c), where θ and ϕ are the polar angles relating $\mathbf{H}_0$ to the crystal axes (a,b,c). Note that such a procedure is necessary because the strong quadrupolar interaction gives rise to a significant angular dependence of $H_{\rm res}$ so that even a misalignment of 1°–2° can cause a significant error ($\sim$30%) in $\mathbf{K}$. The Co shift and EFG were determined by measuring the positions of the central and satellite transitions at fixed field.

Given three nuclei and two possible field orientations for each there are seven distinct magnetic shifts. Note that for

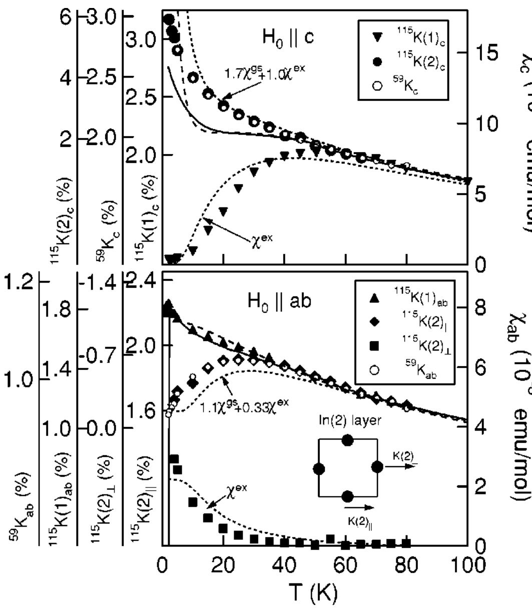

FIG. 1. The magnetic shift versus temperature. The solid lines show χ_c and χ_{ab}. The dashed line is a fit to χ as described in the text; the dotted lines, which have been offset vertically to coincide with the shift scales, are calculations as described in the text. [Note the reversed axis for $^{115}K(2)_\perp$.]

In(1) and Co the magnetic shift is isotropic in the ab plane, whereas for In(2) the shift differs for $\mathbf{H}_0$ parallel or perpendicular to the unit cell face. The temperature dependencies of K for both In sites as well as the Co are shown in Fig. 1, together with χ for both directions. K is a measure of the local electronic spin density at the nuclear site. In general, the shift is given by $K(T)=K_0+\Sigma_i A_i\chi_i(T)$, where K_0 is an orbital shift, independent of the local spin density at the nuclear site and the temperature, and A_i is the hyperfine coupling to χ_i, the ith component of the susceptibility $\chi=\Sigma_i\chi_i$. Both K_0 and A_i can be anisotropic. All of the magnetic shifts except $^{115}K(2)_\perp$ are proportional to χ for $T\gtrsim 40$ K for $\mathbf{H}_0||ab$ and $T\gtrsim 60$ K for $\mathbf{H}_0||c$. Below these temperatures $^{115}K(2)_{||}$, $^{59}K_{ab}$, $^{59}K_c$, and $^{115}K(1)_c$ show dramatic departures from χ. Furthermore, $^{115}K(2)_\perp$ is not proportional to χ in any temperature regime, and exhibits a dramatic downturn below 40 K [note that the axis for $^{115}K(2)_\perp$ is reversed in Fig. 1]. Figure 2 shows K versus χ for both field directions. Note that $K\propto\chi$ for high temperatures ($T>40$ K), and the intercept and slope give K_0 and A, whose values are listed in Table I, where A_{HT} is determined for high temperatures, and A_{LT} for low temperatures. The Co shifts track those of the In(2) for both directions, where $A_c(\mathrm{Co})/A_c(\mathrm{In}(2))=0.26$ and $A_{ab}(\mathrm{Co})/A_\perp(\mathrm{In}(2))=0.33$. Therefore, it seems likely that the Co is not directly coupled to the Ce, but couples to the Ce only via the In(2).

Anomalous departures from $K\propto\chi$ have been known to exist in Ce compounds for several years, although the reason for the departure is still under debate.[9–11] It is generally considered that the Ce $4f$ electron does not have a significant direct overlap with the orbitals of neighboring nuclei. Rather, it is the $6s$ and $5d$ orbitals of the Ce that are hybridized, and the Ce $4f$ moment can create a hyperfine field at a neighboring atom by polarizing the conduction electrons at the Ce site, which is then transferred to the neighbor via an Ruderman-Kittel-Kasuya-Yasida (RKKY) interaction. The conduction electrons at the neighbor then create a hyperfine field at the nucleus via a contact interaction. Two different mechanisms have been proposed to explain the anomalous shift behavior in other heavy fermion systems. In $CeSn_3$ $K(\mathrm{Sn})$ and χ differ below ~ 150 K, and this effect has been ascribed to modifications of the effective hyperfine coupling at the Sn (via the RKKY interaction) by the onset of Kondo compensation below a temperature T_K.[10,12] In $CeCu_2Si_2$ Ohama *et al.* observed that the Cu and Si magnetic shifts also exhibit departures from $K\propto\chi$ below ~ 100 K, and they attribute this behavior to the depopulation of an excited CEF level of the Ce ions ($J=5/2$) and not Kondo coherence.[11] In this case, the overlap between the Ce $4f$ orbitals and the conduction electrons differs depending on the CEF level populations, resulting in temperature-dependent hyperfine couplings to the Cu and Si. In fact, the measured shifts in $CeCoIn_5$ show behaviors similar to those observed in $CeCu_2Si_2$. Namely, the K versus χ plots exhibit positive slope at high temperatures; however, at low temperatures $K\propto\chi$ is recovered, but with a negative slope. Ohama *et al.* attribute the negative hyperfine coupling to an orbital overlap

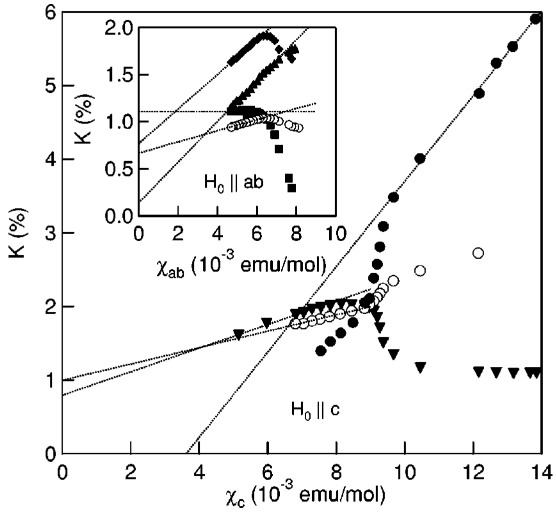

FIG. 2. K versus χ in both directions. The dotted lines are linear fits to the high-temperature data, and the symbols are the same as in Fig. 1.

TABLE I. The hyperfine couplings and orbital shifts of the In(1), In(2), and Co.

Shift_α	K_0(%)	A_{HT} (kOe/μ_B)	A_{LT} (kOe/μ_B)
$\mathrm{In}(1)_c$	0.79(5)	8.94(34)	−0.4(1)
$\mathrm{In}(1)_{ab}$	0.13(4)	12.08(40)	12.08(40)
$\mathrm{In}(2)_c$	−2.10(3)	32.4(3)	22.8(3)
$\mathrm{In}(2)_{\|\|}$	0.76(2)	10.26(17)	−12(1)
$\mathrm{In}(2)_\perp$	1.10(1)	0	−34.7(9)
Co_c	1.00(1)	8.4(5)	6.20(5)
Co_{ab}	0.68(1)	3.30(9)	−4.20(19)

between the ligand s orbital and the Ce $4f$ orbital. They distinguish this direct transferred hyperfine mechanism from that in which the $4f$ moment polarizes the conduction band at the Ce site. According to Ohama *et al.*, the direct contribution can become negative when only the lowest CEF doublet is occupied. Heat capacity data in $CeCoIn_5$ suggest the presence of an excited CEF doublet at ~ 50 K above the ground-state doublet,[3] so it would be reasonable to ascribe the anomalous shift behavior in $CeCoIn_5$ to depopulation of an excited CEF doublet. The strong site dependence of the shift anisotropy in $CeCoIn_5$ also suggests a direct coupling between the In or Co and an anisotropic, localized Ce $4f$ orbital, as in $CeCu_2Si_2$. In both systems the temperature scale for Kondo compensation is much lower than the CEF splitting, suggesting more localized $4f$ character, and the strong directionality of the hyperfine couplings in these materials implies an electronic structure that is more tight binding rather than free-electron-like. Note that for $T > 150$ K $CeCoIn_5$ has a Curie-Weiss susceptibility consistent with a full local moment of the Ce. Although deHaas van Alphen (dHvA) and photoemission data in $CeCoIn_5$ are somewhat consistent with local-density approximation (LDA) calculations that assume the Ce $4f$ electron is itinerant, recent dHvA studies of $Ce_{1-x}La_xRhIn_5$ point to localized f electrons.[13–15] The correlation between the large T_c's and the localized f character of these materials suggests that the local moments, which could be a source for spin fluctuations, are essential for the development of heavy fermion superconductivity.[16,17]

In order to investigate the possible role of CEF effects we have fit χ to extract the CEF parameters. The dashed lines in Fig. 1 show a fit to the expression $\chi^{-1} = \chi_{\rm CEF}^{-1} + \lambda$, where $\chi_{\rm CEF}$ is the CEF susceptibility for the Ce ion, and λ is a molecular field term. The Ce ion in $CeCoIn_5$ experiences a crystal field with tetragonal symmetry, so $\mathcal{H}_{\rm CEF} = b_2^0 O_2^0 + b_4^0 O_4^0 + b_4^4 O_4^4$, where the O_n^m are the Steven's operators.[18] In this field the $J = 5/2$ manifold is split into three doublets $(\Gamma_6, \Gamma_7^{(1)}, \Gamma_7^{(2)})$, where the wave functions are given by $|\pm\frac{1}{2}\rangle$, $\mp\sin\alpha|\pm\frac{3}{2}\rangle \mp\cos\alpha|\mp\frac{5}{2}\rangle$, $\mp\cos\alpha|\pm\frac{3}{2}\rangle \pm\sin\alpha|\mp\frac{5}{2}\rangle$, and $\chi_{\rm CEF} = [\partial^2(\ln Z)/\partial H^2]_{H=0}$. Here Z is the partition function for the Hamiltonian $\mathcal{H}_{\rm Ce} = \mathcal{H}_{\rm CEF} + g_J \mu_B \mathbf{H}\cdot\mathbf{J}$, where $g_J = 6/7$, μ_B is the Bohr magneton, and $\mathbf{J}$ is the spin operator for $J = 5/2$. We find the best fit for the Γ_6 ground state ($J_z = \pm\frac{1}{2}$), with excited states at 34 and 102 K above the ground state, $\alpha = 1.47$, and an anisotropic molecular field: $\lambda_c = 18.8$ mol/emu and $\lambda_{ab} = -113.2$ mol/emu.[19] The anisotropy of λ reflects Ce-Ce couplings which differ for neighbors in and out of the plane. The fit reproduces the plateau feature, and suggests that the anomalous behavior of the magnetic shifts below 50 K may also be explained by changes in the hyperfine couplings as the excited CEF states are depopulated. Note, for example, that in Fig. 2 $^{115}K(1)_c$ appears to be independent of χ_c at low temperatures. This behavior suggests that $^{115}K(1)_c$ couples only to the excited CEF states. If we decompose $\chi_{\rm CEF} = \chi_{\rm CEF}^{\rm gs} + \chi_{\rm CEF}^{\rm ex}$ into contributions from the ground-state doublet and from the excited doublets, one might then expect $K = K_0 + A_{\rm gs}\chi^{\rm gs} + A_{\rm ex}\chi^{\rm ex}$, where $(\chi^i)^{-1} = (\chi_{\rm CEF}^i)^{-1} + \lambda$. We determine $\chi_{\rm CEF}^{\rm gs}$ ($\chi_{\rm CEF}^{\rm ex}$) by suppressing the field dependence of the excited (ground) state energy levels in the expression for Z. By adjusting K_0, $A_{\rm gs}$, and $A_{\rm ex}$ appropriately, we can qualitatively explain the temperature dependence of all the shifts in Fig. 1 (dotted lines). Note that $\chi_{\rm CEF}^{\rm ex} < 0$ in the ab plane, so for this component the absolute value of λ_{ab} was used.

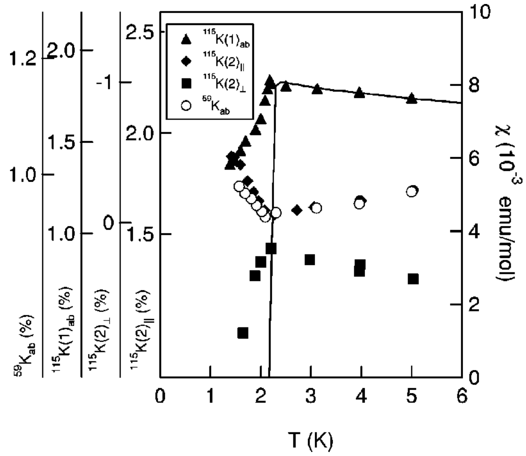

FIG. 3. The magnetic shift for $\mathbf{H}_0 || ab$ in the superconducting state. The solid line is the bulk susceptibility, which becomes fully diamagnetic below 2.3 K.

The anomalous behavior of the shifts might also be explained by two components of χ with a different origin than crystal field states. However, there is only one Ce site in the unit cell, and susceptibility and heat capacity data indicate that the observed properties can be entirely attributed to the Ce (i.e., Co is nonmagnetic in $CeCoIn_5$). Therefore it seems likely that the two components can only be attributed to different CEF states on the Ce ions. It is interesting to note that measurements of the In(1) shift in the isostructural compound $CeRhIn_5$ reveal a positive hyperfine coupling for $4\ {\rm K} < T < 50$ K, with no signs of the dramatic departure from $K \propto \chi$ seen in $CeCoIn_5$.[20] Clearly, if the hyperfine anomaly is the only mechanism at work in $CeCoIn_5$ then the CEF parameters in $CeCoIn_5$ must differ significantly from those in $CeRhIn_5$. In fact, recent work by Takeuchi *et al.* suggests that the ground-state CEF level in $CeRhIn_5$ is Γ_7 rather than Γ_6.[21]

Below T_c χ is dominated by the diamagnetic response, masking the intrinsic behavior of the spin susceptibility. K, however, couples only to the spin susceptibility and provides a direct measure of $\chi^{\rm spin}$ in the superconducting state. The temperature dependencies of the shifts for both In sites as well as the Co in $CeCoIn_5$ are shown in Fig. 3 for $\mathbf{H}_0 || ab$ down to 1.4 K. Because of the thin platelet morphology of $CeCoIn_5$, demagnetization fields in the superconducting state can be significant for $\mathbf{H}_0 || c$, precluding an accurate determination of the magnetic shift since the local field at the nucleus is poorly determined. We estimated that for our sample, the demagnetization factor for $\mathbf{H}||c$ is $N_c/4\pi \approx 0.79$. Therefore, although we observe a decrease in the resonance frequencies for this direction one cannot resolve whether the decrease is due to a change in K or to a change in H_0 internally. However, for $\mathbf{H}_0 || ab$ the demagnetization factor is much smaller, so the internal field below T_c is

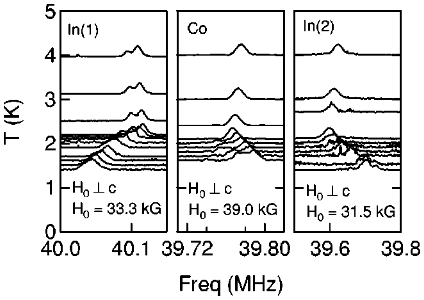

FIG. 4. Spectra of the In(1), Co, and In(2) at various temperatures through T_c. The In(2) spectrum is for $\mathbf{H}_0$ normal to the unit cell face. The two peak structure of the In(1) spectrum indicates the presence of two slightly differently oriented crystals in the sample.

known to a greater degree of accuracy. Therefore, we only present data on the shifts for the field in the plane.

The decrease in ${}^{115}K(1)_{ab}$ seen in Fig. 3 implies a decrease in χ^{spin}. However, ${}^{59}K_{ab}$, ${}^{115}K(2)_{\perp}$, and ${}^{115}K(2)_{||}$ *increase* below T_c [note the reversed axis for ${}^{115}K(2)_{\perp}$ in Fig. 3]. Spectra of the In(1), In(2), and Co at different temperatures are shown Fig. 4, clearly exhibiting the behaviors seen in Fig. 3. An increase of the absolute value of ${}^{115}K(2)_{\perp}$, ${}^{115}K(2)_{||}$, and ${}^{59}K_{ab}$ below T_c can be understood by recognizing that the hyperfine coupling is negative below 50 K (see Fig. 3), so an increase in K implies a decrease in χ^{spin}. Thus, all of the shifts for $\mathbf{H}\perp c$ are consistent with a decrease in χ^{spin}, implying spin-singlet pairing of the Cooper pairs in the superconducting state. Given the recent heat capacity and thermal conductivity measurements revealing higher orbital symmetry,[4,22] we can conclude that the order parameter in $CeCoIn_5$ has *d*-wave symmetry. During the course of this work, we became aware of similar work by the group of Kohara[23] who report magnetic shift results below T_c. Although our conclusions about singlet pairing are the same, the temperature dependencies of the shifts differ.

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