Absence of the Pauli-Paramagnetic Limit in a Superconducting $U_6Co$

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We performed $^{59}Co$ nuclear magnetic resonance (NMR) measurements of single-crystalline $U_6Co$. There is a small decrease in the Knight shift in the superconducting (SC) state, but this change mainly arises from the SC diamagnetic effect. The negligible change of the spin part of the Knight shift, together with the absence of the Pauli-paramagnetic effect in the SC $U_6Co$, is understood as a consequence of the small spin susceptibility. The nuclear spin-lattice relaxation rate $1/T_1$ is also measured in the SC state under the magnetic field, and exhibits a tiny Hebel-Slichter peak just below the SC transition temperature and exponential behavior at lower temperatures. These behaviors are in agreement with the full-gap s-wave pairing in $U_6Co$.

Uranium compounds $U_6X$ ($X = Mn, Fe, Co, and Ni$) are superconductors with relatively high superconducting (SC) transition temperatures $T_c$ among the uranium-based compounds. Contrary to other uranium-based heavy-fermion systems including ferromagnetic superconductors, $5f$ electrons in $U_6X$ compounds exhibit an itinerant nature even at room temperature, and do not exhibit magnetic ground states. The SC properties are consistent with the conventional one: for instance, the full-gap superconductivity of $U_6Co$ ($T_c = 2.33K$) has been indicated by the penetration depth, nuclear spin-lattice relaxation rate $1/T_1$ and more recently, by specific heat measurements. Thus, at present, these compounds are good reference systems for the uranium-based unconventional superconductors.

It has been suggested that the superconductivity of $U_6X$ might be close to ferromagnetism because the total magnetic susceptibility of these compounds is so large that it is comparable to that of the nearly ferromagnetic metal Pd. This can be interpreted as a sign of the strongly enhanced electronic spin susceptibility owing to the electronic correlation. However, the magnetic properties of $U_6X$ in the normal state are quite different from those of ferromagnetic superconductors in which ferromagnetic instability is commonly observed, while it is usually unfavorable for conventional superconductivity. Therefore, it is necessary to determine whether $U_6X$ compounds are close to the ferromagnetism and to consider the origin of the large magnetic susceptibility in them.

It is also noteworthy that SC $U_6Co$ has a large upper critical field $H_{c2}$ for $T_c$. In spin-singlet superconductors, the superconductivity is limited by the Pauli-paramagnetic effect under a magnetic field. This is because the spin susceptibility decreases in the SC state, and the energy difference between the SC and the normal states reduces under a larger magnetic field due to the magnetic energy in the normal state. The Pauli-limiting field $H_P$ is expressed as $\mu_0 H_P / T = 1.86(2/g)T_c / K$ in the weak-coupling BCS model, where $g$ is the $g$-factor. If this is applied to $U_6Co$ assuming $g = 2$, $\mu_0 H_P = 4.3 T$ is obtained. However, $\mu_0 H_{c2}$ along the [001] and [110] directions in $U_6Co$ in the tetragonal structure is 7.85 and 6.56 T, respectively and both of them exceed 4.3 T. The Pauli-paramagnetic effect is actually absent in $U_6Co$. The large $H_{c2}$ value has been considered to originate from the small $g$-factor.

In this paper, we report $^{59}Co$ NMR measurements of $U_6Co$, which are performed to further investigate the electronic spin susceptibility from a microscopic point of view. We found that the NMR Knight shift exhibits a small decrease in the SC state. This result suggests that the spin susceptibility of $U_6Co$ is not a dominant term in the total susceptibility, but that the Van Vleck term is a main term.

We used a single-crystalline $U_6Co$ sample with $T_c = 2.34K$ for the NMR study. The sample was cooled using 4He or a 3He-4He dilution refrigerator. $^{59}Co$ NMR was performed with the magnetic field perpendicular to the [001] direction, and the Knight shift and $1/T_1$ were measured. Since the $^{59}Co$ nucleus has $I = 7/2$ spin and the Co site does not have cubic symmetry, the NMR spectrum splits into 7 lines owing to a nuclear quadrupole interaction. All the NMR data were measured at the central line ($1/2 \leftrightarrow -1/2$). The magnetic field was calibrated using a $^{63}Cu$ signal arising from the NMR coil. In addition to NMR measurements, we performed nuclear quadrupole resonance (NQR) measurements of a powdered single-crystalline sample to obtain information about the homogeneity of the crystal structure.

Figure 1 shows the $^{59}Co$ NQR spectrum of the powdered sample. The quadrupole frequency is estimated as $\nu_Q \simeq 1.77 MHz$ for the present sample. The asymmetric parameter $\eta$ is almost 0, which is consistent with the fact that the electric field gradient at the Co site has axial symmetry with respect to the [001] direction. The value of $\nu_Q$ in this sample is slightly larger and the line width is broader than those in the previous NQR study. Nevertheless, a clear SC anomaly is observed in the single-crystalline sample, as mentioned later, and...
thus, the present samples are suitable for studying the superconductivity of U$_6$Co.

The $1/T_1$ values in U$_6$Co at 1.00 T are shown in Fig. 2. A Hebel-Slichter (HS) peak is found just below $T_c$ as observed in the previous NQR measurement under zero magnetic field,[3] although the HS peak is more strongly suppressed than that in the previous NQR. This result again indicates that U$_6$Co is an $s$-wave superconductor. The HS peak is slightly larger at 0.70 T than at 1.00 T, indicating that the peak is suppressed by the magnetic field. Figure 3 shows $T_{ls}/T_{1n}$ against $T_c(H)/T$, where $1/T_{ls}$ (1/$T_{1n}$) is the relaxation rate in the SC (normal) state. An exponential decrease of $1/T_1$ is observed at lower temperatures, although the relaxation curves have a short-$T_1$ component in the SC state arising from the vortex core. The $1/T_1$ value shown in Figs. 2 and 3 corresponds to a longer-$T_1$ component. The calculation based on the $s$-wave full-gap model, and they reproduce the experimental result in $T \leq 0.5T_c$. The density of states (DOS) in the SC state is broadened by a rectangle function with a width of $2\delta$ and a height of $1/2\delta$ for the calculation of $1/T_1$. The calculated $1/T_1$ and DOS are expressed as follows:

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\frac{T_{1n}}{T_{ls}} = \frac{2}{k_B T} \int_0^\infty [N_s(E)]^2 \left( 1 + \frac{\Delta^2}{E^2} \right) f(E)[1-f(E)] dE,$n(E) = \frac{1}{2\delta} \int_{E-\delta}^{E+\delta} \frac{E'}{(E'^2 - \Delta^2)^{1/2}} dE'.

The SC gap $\Delta$ is set to $2\Delta/k_BT_1(H) = 3.7$ from Ref. [3] and $\delta/\Delta = 0.44$. The strong suppression of the HS peak just below $T_c$ is not reproduced even with the relatively large $\delta$ and may be ascribed to the magnetic field. Recently, the Doppler shift effect, or the so-called Volovik effect, has been proposed as a mechanism of the suppression of the HS peak of the $s$-wave superconductor under the magnetic field.[8] The Volovik effect has been regarded as a minor effect on the low-energy excitation of quasi-particles in the case of full-gap superconductors, but this cannot be neglected for the HS peak, because it is sensitive to the edge form of the SC DOS particularly just below $T_c$. Therefore, it is considered that the suppression of the peak in U$_6$Co under the magnetic field could be explained by the Volovik effect.

$1/T_1$ of U$_6$Co in the normal state exhibits the Korringa relation with $1/T_1T \approx 2.0 \text{s}^{-1}\text{K}^{-1}$ just above $T_c$, as seen in the inset of Fig. 2 and this value is not strongly enhanced compared with other uranium-based heavy-fermion systems. For instance, this is quite smaller than that of the itinerant ferromagnetic superconductor UC$_4$Ge: $1/T_1T \approx 10^2-10^3 \text{s}^{-1}\text{K}^{-1}$ in the paramagnetic state under zero magnetic field depending on the temperature.[9] Instead, $1/T_1T$ of U$_6$Co is close to that of
$^{59}$Co $1/T_1T$ in YCoGe, which is a nonmagnetic reference compound of UCoGe: $1/T_1T = 2.03\text{s}^{-1}\text{K}^{-1}$ (Ref. 10). The ordinary $1/T_1T$ value in the normal state implies that the SC phase of U$_6$Co is not in proximity to the ferromagnetic ground state.

The Knight shifts of U$_6$Co at several fields below 4.2 K are shown in Fig. 4 (a), and the NMR spectra at 1.00 T are shown in Fig. 4 (b). The decrease in the Knight shift extrapolated to $T = 0$ is $\simeq 0.039 \pm 0.005\%$ ($1.00\text{T}$), $0.009 \pm 0.005\%$ ($2.00\text{T}$), and $0.002 \pm 0.005\%$ ($3.00\text{T}$), and these values are much smaller than the total Knight shift of $\sim 1.7\%$. In general, the Knight shift decreases due to a diamagnetic field $H_{\text{dia}}$ as well as a decrease in the spin susceptibility in the SC state. $H_{\text{dia}}$ is roughly expressed as $H_{\text{dia}} \simeq H_{c1} \log(H_{c2}/H)/(2 \log \kappa)$ (defined as positive), where $H_{c1} \ll H \ll H_{c2}$. $H$ is the external field, $\kappa$ is a Ginzburg-Landau parameter, and $H_{c1}$ is the lower critical field. Therefore, the diamagnetic shift $K_{\text{dia}} = H_{\text{dia}}/H$ is strongly suppressed with increasing $H$.

On the other hand, the spin part of the Knight shift is $K_s(0)/K_s(T > T_c) \simeq aH/H_{c2}$ at lower fields ($a$ is close to unity), and thus the Knight-shift change arising from the spin part does not strongly depend on $H$ as long as $H/H_{c2} \ll 1$. The experimental Knight-shift decrease is suppressed with increasing $H$ even well below $H_{c2}$ and this is qualitatively similar to the behavior of $K_{\text{dia}}$. In addition, the field dependence of the Knight-shift decrease is roughly reproduced with a theoretical formula of the diamagnetic field, which is valid in a wide range of the fields as shown in Fig. 4 (b). Here, we adopt $\kappa = 86$ for the best fit of the experiment, which is close to $\kappa \simeq 70$ estimated from $H_{c2}$ and the thermodynamic field. This also suggests that the diamagnetic effect is a dominant origin of the Knight-shift change in U$_6$Co.

The magnitude of $K_s$ could not be properly determined in this study, but there is a constraint on the value of $K_s$, as discussed below. Noting that $K_{\text{dia}}$ decreases faster than $H^{-1}$ against $H$, and assuming that $a \simeq 1$ for $K_s(0)$, then $K_s$ in the normal state satisfies $-0.05\% \lesssim K_s \lesssim 0.01\%$. The lower limit is not quite strict because the concrete form of $H_{\text{dia}}(H)$ is not assumed, and the upper limit is obtained by the Knight-shift change at 3.00 T. Therefore, this constraint on $K_s$ does not necessarily mean that a negative $K_s$ is more likely than a positive one.

Here, we attempt to estimate how the Knight shift would behave when the Pauli-paramagnetic effect is absent in U$_6$Co. Since the magnetic susceptibility is temperature-independent in the normal state, the hyperfine coupling constant $A_{hf}$ cannot be determined.
through a comparison between the susceptibility and the Knight shift. Thus, we tentatively adopt $A_{hf} \approx 3\, \text{T}/\mu_B$ for the $^{59}\text{Co}$ hyperfine coupling constant in $U_6\text{Co}$, which is a typical value for $^{59}\text{Co}$ in uranium-based compounds such as UCo$_3$.[13] and UCoAl[14] This is based on the assumption that the U $5f$ electrons are transferred to the Co $4s$ electrons, and the contribution of the Co $3d$ electrons is relatively small. Considering the absence of the Pauli-paramagnetic effect, $H_P$ satisfies $H_P = H_c/\sqrt{\Delta \chi_s} > H_c$, where $\Delta \chi_s$ is the decrease of the spin susceptibility in the SC state (a volume susceptibility in SI units for calculating $H_P$) and $H_c$ is the thermodynamic field. Using $\mu_0 H_c = 0.065\, \text{T}$ at 0K (Ref. [9] and the lattice parameter[15] of $U_6\text{Co}$, $\Delta \chi_s \lesssim 0.7 \times 10^{-4}\, \text{emu}/\text{U-mol}$ is deduced, which is much smaller than the total value $\chi = 5.3 \times 10^{-4}\, \text{emu}/\text{U-mol}[6]$. Thus the Knight-shift change in a spin part is estimated as $\Delta K_s = A_{hf} \Delta \chi_s / N_A \mu_B \lesssim 0.04\%$, where $N_A$ is Avogadro’s number, and $\mu_B$ is the Bohr magneton. The actual change of the Knight shift after subtracting the diamagnetic effect is sufficiently less than this limit.

It is known that the Knight-shift decrease is suppressed by spin-orbit scattering in the dirty-limit superconductors.[16,17] In the case of $U_6\text{Co}$, since the mean free path is estimated to be on the same order of the BCS coherence length, this mechanism plays a minor role in the suppression of the Knight shift change. Although the above discussion is based on the assumption that $A_{hf}$ is positive and not very small, the small spin susceptibility is a promising origin of the small Knight-shift change in $U_6\text{Co}$. The absence of the Pauli-paramagnetic effect is closely related to the Knight-shift behavior in the SC state in $U_6\text{Co}$.

In some uranium-based superconductors such as UPt$_3$[18] and URu$_2$Si$_2$[19], the Knight-shift change due to SC pairing is much smaller than the total value. This means that the large part of the Knight shift is not related to the quasiparticles at the Fermi energy $E_F$. This also applies to $U_6\text{Co}$: $1/T_1T$ slightly depends on the temperature as seen in the inset of Fig. 2 reflecting the structure of the DOS around $E_F$, while such a temperature-variation is not seen at all in the magnetic susceptibility of $U_6\text{Co}$[6] and in the present Knight shift at 12.0 T (not shown). This indicates that the spin part of the Knight shift and spin susceptibility are quite small in total. Therefore, the spin state of the SC pairing should be carefully discussed when the Knight-shift change is absent in uranium-based superconductors.

The small spin susceptibility of $U_6\text{Co}$ is also inferred from a comparison among $U_6\text{X}$ compounds. The discussion here is based on Table VII in Ref. [7] and some of the data are shown in Fig. 3. The electronic specific heat coefficient of $U_6\text{X}$ varies between $\gamma = 15$–26 mJ/(K$^2$ U-mol), and the compound with a larger $\gamma$ has a higher $T_c$. This tendency is consistent with the BCS theory, in which a larger DOS at $E_F$ is more favorable for the superconductivity. However, the total susceptibilities of $U_6\text{X}$ compounds are similar (approximately $5 \times 10^{-4}\, \text{emu}/\text{U-mol}$ in the powder samples), and this suggests that most of the susceptibility is independent of the quasiparticles around $E_F$. It seems that the Van Vleck term should make a dominant contribution to the susceptibility in these systems. The small spin susceptibility is consistent with the small $g$-factor[3] and this is not surprising if the strong spin-orbit coupling in actinides is taken into consideration.[20]

Finally, we comment on the present Knight shift in $U_6\text{Co}$. A positive $A_{hf}$ and thus, positive $K_s$ are assumed in the above discussion for simplicity, but this is not actually evident since the Co $3d$-electronic spins would lead to negative hyperfine coupling owing to core polarization if they have finite DOS at $E_F$. If the core polarization is a dominant mechanism in the spin part of the Knight shift, $A_{hf}$ should be negative. In this case, the Knight shift could shift to larger values in the SC state depending on the magnitude of $A_{hf}$, which is not experimentally detected in the present field ranges. There is even a possibility that the positive Co $4s$ and negative $3d$ contributions cancel each other, as seen in V metal[21] and the spin part of the Knight shift might remain constant in the SC state even if the spin susceptibility is sufficiently large for the Pauli-paramagnetic effect to occur. As for the orbital part of the $^{59}\text{Co}$ Knight shift in $U_6\text{Co}$, this does not necessarily originate only from the U $5f$ Van Vleck terms. Co $3d$ electrons also produce the orbital part of the Knight shift depending on the band occupancy. These issues can be resolved if the band structure of $U_6\text{Co}$ is clarified.

In summary, we performed $^{59}\text{Co}$ NMR measurements on a single crystal of $U_6\text{Co}$, and found that the Knight-shift change in the SC state is small compared with the total Knight shift. This result, as well as the large upper critical field, can be understood to occur because the spin susceptibility is much smaller than the total susceptibility. The absence of the Pauli-paramagnetic effect is likely
to be associated with the negligible change in the Knight shift in this system. The value of the expected Knight-shift change in the SC state was estimated by using the plausible value of the hyperfine coupling constant. The $1/T_1$ behavior in the SC state is in good agreement with the s-wave full gap of $U_6Co$.

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