# Magnetic resonance of heavy-fermion superconductors and high-$T_c$ superconductors

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Recently there has been a great deal of interest in two classes of superconductors, heavy-fermion superconductors and high-$T_c$ copper oxide superconductors. The behavior and nature of superconductivity in these two classes of materials are reviewed, and their similarities and differences are noted. The temperature dependences of the spin-lattice relaxation time ($T_1$) and the spin-spin relaxation time ($T_2$) of $^9$Be in $UBe_{13}$ are quite similar to those of $^{63}$Cu and $^{89}$Y in $YBa_2Cu_3O_{7-\delta}$. The Knight shift of $UBe_{13}$ is unchanged during the superconducting phase transition. The Knight shift of $YBa_2Cu_3O_{7-\delta}$ changes from the value in the normal state $K_n/K_s=1$ at $T\gtrsim T_c$ to $K_n/K_s=0.5$ at $T=6$ K. Both do not approach zero as expected in BCS theory. This strongly suggests that the pairing mechanism which induces superconductivity in heavy-fermion materials might also be involved in high-$T_c$ superconductors.

## I. INTRODUCTION

The two kinds of superconductors which have been discovered recently, heavy-fermion superconductors[1–3] and high-$T_c$ oxide superconductors,[4–7] display exotic properties. The mechanisms of electron pairing in these superconductors have evoked lively debates among theorists and experimentalists alike. Several alternative mechanisms to the conventional Bardeen-Cooper-Schrieffer (BCS) theory have been discussed recently.[8]

The heavy-fermion superconductors, $CeCu_2Si_2$, $UBe_{13}$, and $UPt_3$, exhibit enormous values of the linear specific-heat coefficient $\gamma$. As determined by this coefficient, the effective mass $m^*$ of the band electron is more than 2 orders of magnitude greater than the free-electron mass $m_e$. Since the discontinuous jump in the specific heat at the superconducting transition temperature $T_c$ is of the order of $T_c$, the heavy fermions themselves condense into the superconducting ground state. The possibility of unconventional Cooper pairing has been raised[9] in these materials, with non-BCS orbital and spin symmetries and strong energy-gap anisotropy.

In *R*-Ba-Cu-O compounds, the unexpected high $T_c$'s ($>95$ K) of these copper oxide materials also suggests the possibility that these materials exhibit an unconventional type of superconductivity, rather than the ordinary electron-phonon interaction. Although the high-$T_c$ superconductors have very high values of $T_c>95$ K, many of their superconducting properties exhibit the power-law behavior which also appears in heavy-fermion superconductors. It is possible that the extraordinary types of superconductivity displayed by these two classes of materials have a common origin.[10]

In this paper, we compare NMR (nuclear magnetic resonance) measurements of the heavy-fermion superconductor $UBe_{13}$ and the high-$T_c$ copper oxide superconductor $YBa_2Cu_3O_{7-\delta}$.

## II. SPIN-LATTICE RELAXATION

NMR was used to explore superconductivity before the appearance of the BCS theory.[11] The value of NMR lies in its sensitivity to the behavior of the local microscopic magnetic field, both static and dynamic, in condensed matter. Nuclear spin-lattice relaxation, the process in which a nuclear spin population distribution attains thermal equilibrium with the lattice, is due to the coupling between nuclear spins and low-lying thermal excitations. In metals, the dominant mechanism for nuclear spin-lattice relaxation is often the so-called Korringa mechanism, in which conduction electrons are spin-flip scattered by nuclear moments. In the superconducting state, the conduction electrons condense into a pairwise occupation of the Bloch state $|\mathbf{k},\sigma\rangle$. If $|\mathbf{k},\sigma\rangle$ is occupied, so is its mate $|-\mathbf{k},-\sigma\rangle$. This coherent occupation of the condensed state puts limitations on scattering processes, and, in addition, alters the number of excited-state electrons available for scattering. In nuclear magnetic relaxation, the perturbation which describes the transition rate for scattering is not time-reversal invariant. In light of this property, Schrieffer[12] found that to derive the transition rate of scattering for the superconducting state, one must multiply the transition rate in the normal state by the factor

$$C(\mathbf{k},\mathbf{k}')=\tfrac{1}{2}[1+(\Delta^2/E_{\mathbf{k}}E_{\mathbf{k}'})]\,. \qquad (1)$$

Consider, for simplicity, a nuclear spin of $\frac{1}{2}$ and an experiment performed in a magnetic field with nuclear Zeeman energy $\hbar\omega$. If the only coupling between the conduction electrons and the nuclei is the hyperfine contact interaction, then the Hamiltonian can be written as

$$\mathcal{H}_0=(8\hbar/3)\,|U_{kF}(0)|^2\mathbf{I}\cdot\mathbf{S}\,, \qquad (2)$$

where **I** and **S** are spin operators for nuclear and electronic spins, respectively, and $U_{kF}(0)$ is the Bloch function amplitude at the nuclear site. By Fermi's "golden rule," the transition rate $W$ between $S=\frac{1}{2}$ to $S=-\frac{1}{2}$ is given by

$$W=(\pi/2\hbar)[(8\pi/3)\,|U_{kF}(0)|^2]\sum_{\mathbf{k},\mathbf{k}'}C(\mathbf{k},\mathbf{k}')f_{\mathbf{k}}(1-f_{\mathbf{k}'})[\delta(E_{\mathbf{k}}-E_{\mathbf{k}'}-\hbar\omega)+\delta(E_{\mathbf{k}}-E_{\mathbf{k}'}+\hbar\omega)]\,. \quad (3)$$

The Fermi-Dirac distribution function $f_{\mathbf{k}}$ accounts for the thermal population of excited initial states, and $(1-f_{\mathbf{k}'})$ gives the thermal depopulation of final states required by the Pauli principle. The $\delta$-function factor accomplishes the conservation of total energy in the scattering event, where both the electron and nuclear spin are flipped by the interaction. The sums over $\mathbf{k}$ and $\mathbf{k}'$ can be converted to integrals using the BCS density of states

$$N_{\mathrm{BCS}}(E)=N(0)\,|E\,|/(E^2-\Delta^2)^{1/2}\,. \quad (4)$$

If so, then the ratio of relaxation rates

$$R_s/R_n=T_{1n}/T_{1s}\,, \quad (5)$$

is found to be

$$R_s/R_n=\frac{2}{k_BT}\int_{\Delta}^{\infty}(EE'+\Delta^2)f(E)[1-f(E')]/[(E^2-\Delta^2)(E'^2-\Delta^2)]^{1/2}dE\,,\quad E'=E\pm\hbar\omega\,, \quad (6)$$

where $T_{1n}$ and $T_{1s}$ are spin-lattice relaxation time at normal states and superconducting states, respectively.

If the difference in energy between final and initial electron states is ignored, the integral diverges logarithmically at $E=\Delta$. This disturbing result is a consequence of the singular nature of $N_{\mathrm{BCS}}(E)$. In real materials the singularity will be removed by some mechanisms, and it is possible at this early point to see that spin-lattice relaxation measurements can yield information on the nature of such a mechanism. Assuming that the singularity has been removed, the behavior of the relaxation rate will be divided into two regimes, according to whether $\Delta$ is greater or smaller than $k_BT$. In the former regime, the Fermi-Dirac factor will be nearly exponential and rapidly vary for $E\geq\Delta$. Only the state near the gap threshold will be appreciably populated, and the relaxation rate will behave essentially as $\exp(-\Delta/k_BT)$. For $\Delta<k_BT$, near the transition temperature $T_c$, the states which contribute to the peak at $E=\Delta$ will uniformly populate, such that the relaxation rate $R_s$ will, in general, increase over the value of $R_n$ at $T_c$. It is clear that Eq. (3) underestimates the observed $T_1$, as would be expected if some mechanism removes the BCS singularity in the density of state. Hebel and Slichter[13] proposed a phenomenological broadening in the energy of the excited states. The appropriate generalization of Eq. (3) in this case is

$$R_s/R_n=\frac{2}{k_BT}\int_{\Delta}^{\infty}[N_s^2(E)+M_s^2(E)]f(E)[1-f(E)]dE\,, \quad (7)$$

where the "normal" density of states $N_s(E)$ is

$$N_s(E)=\int B(E'-E)E'/(E'^2-\Delta^2)^{1/2}dE'\,, \quad (8)$$

and the "anomalous" density of states is defined as

$$M_s(E)\int B(E'-E)\Delta/(E'^2-\Delta^2)^{1/2}dE'\,. \quad (9)$$

$B(E'-E)$ is a broadening function which is usually chosen to be a rectangle centered around $E'=E$ for computational simplicity. In the anisotropic condensed state, $N_s(E)$ can be written as[14]

$$N(E)=\frac{N_0|E\,|}{4\pi}\int\int_A d\Omega/[E^2-C(\theta,\phi)^2]^{1/2}\,, \quad (10)$$

where $N_0$ is the normal-state density of states at the Fermi level. The above integral is extended over the spherical region $A$, where $|C(\theta,\phi)|$ is smaller than $E$. The generalized gap function $C(\theta,\phi)$ is related to the individual-particle excitation energy

$$E_{\mathbf{k}}=[\epsilon_{\mathbf{k}}^2+C(\theta,\phi)^2]^{1/2} \quad (11)$$

and, for orbital angular momentum $L=0$, $C(\theta,\phi)=\Delta=\mathrm{const}$, such that the corresponding spectrum has a gap of $2\Delta$. However, for $L\neq0$, $C(\theta,\phi)$ may vanish for some directions, so that the energy spectrum does not exhibit a true gap, but only a sharp reduction of the density of state near the Fermi level. For the polar-state model[15] for $L=1$ triplet pairing,

$$C(\theta,\phi)=\Delta\cos\theta\,; \quad (12)$$

therefore, when $E<\Delta$,

$$N_s(E)=\frac{N_0E}{4\pi}\int\int_A d\Omega/(E^2-\Delta^2\cos^2\theta)^{1/2}=\frac{N_0\pi E}{2\Delta}\,. \quad (13)$$

Since

$$M(E)=\frac{1}{4\pi}\int\int_A\frac{\Delta\cos\theta}{(E^2-\Delta^2\cos^2\theta)^{1/2}}d\Omega=0\,, \quad (14)$$

we have

$$[N_s^2(E)+M^2(E)]/T^2\propto(E/T)^2 \quad (15)$$

and

$$T_1^{-1}\propto T^3\int d(E/T)f(E)\times[1-f(E)][N_s^2(E)+M^2(E)]/T^2\,. \quad (16)$$

Since $f(E)$ is a function of $E/T$,

$$\int d(E/T)f(E)[1-f(E)][N_s^2(E)+M^2(E)]/T^2=\mathrm{const}\,, \quad (17)$$

and $T_1^{-1} \propto T^3$. When $E > 0$,

$$N_s(E) = N_0 E \int \frac{d\cos\theta}{(E^2 - \Delta^2\cos^2\theta)^{1/2}} = \left[\frac{N_0 E}{\Delta}\right] \sin^{-1}\frac{\Delta}{E} . \tag{18}$$

In the axial-state model[15] for $L=1$ triplet pairing, $C(\theta,\phi) = \Delta\sin\theta$; therefore,

$$N_s(E) = \frac{N_0 |E|}{2} \ln\left|\frac{(E+\Delta)}{(E-\Delta)}\right| \tag{19}$$

for $E < 0$, and

$$T_1^{-1} \propto T \int dE f(E)[1-f(E)] \left[\ln\left|\frac{(E+\Delta)}{(E-\Delta)}\right|\right]^2 . \tag{20}$$

In the low-temperature limit, where $E/\Delta \rightarrow 0$, we have

$$N_s(E) \simeq N_0 (E/\Delta)^2 , \tag{21}$$

such that

$$T_1^{-1} \propto T^5 \int d\left[\frac{E}{T}\right] f(E)[1-f(E)] \frac{E^4}{T^4} ; \tag{22}$$

therefore,

$$T^{-1} \propto T^5 . \tag{23}$$

Only those states for which the generalized gap function $C(\theta,\phi)$ approaches zero will contribute to the low-lying excitation states. If $C(\theta,\phi)$ vanishes at some lines on the Fermi surfaces, then the behavior of the gap function near those lines might be the same and yield the same energy dependence of the density of states. Furthermore, if $C(\theta,\phi) = \Delta\cos\theta$, the gap function vanishes for the line whose $\theta = \pi/2$. Therefore, if $C(\theta,\phi) = 0$ at an arbitrary line on the Fermi surface, then $C(\theta,\phi)$ behaves like $\Delta\cos\theta$ near the line, such that $N_s(E) \propto (E)$ and $T_1$ follows a $T^3$ law. Thus, the $T^3$ power-law dependence of the relaxation rate is generally valid for an anisotropic superconductor where $C(\theta,\phi)$ vanishes linearly at lines on the Fermi surface, rather than being valid only where $C(\theta,\phi) = \Delta\cos\theta$. Similarly, as long as $C(\theta,\phi)$ vanishes linearly at points on the Fermi surface, $N_s(E)$ is proportional to $E^2$ and $1/T_1$ is proportional to $T^5$ at low energy.

The temperature dependence of the $^9$Be nuclear spin-lattice relaxation time $T_1$ in the $UBe_{13}$ is shown in Fig. 1. The frequency used to measure $T_1$ was 9 MHz, and the corresponding magnetic field was 15.5 KOe. The superconducting transition temperature $T_c$ determined by the $T_1$ measurement is near 0.72 K which is somewhat lower than $T_c(\chi_{ac}) \simeq 0.78$ K, as determined by the ac susceptibility transition. Just above $T_c$, the $T_1$ data follow the Korringa relation, $1/T_1T \simeq 2\times10^{-1}$ $s^{-1}K^{-1}$, which is expected in a normal Fermi liquid well below the degeneracy temperature $T_F$. In the superconducting state, the measurements of $1/T_1$ are consistent with $T^3$ temperature dependence for 0.2 K $< T < T_c$. Below 0.16 K, $(TT_1)^{-1} \simeq 5\times10^{-3}$ $(Ks)^{-1}$. The deviation from the power law below 0.2 K might be due to paramagnetic impurities. If the power-law behavior of $1/T_1$ is an intrinsic

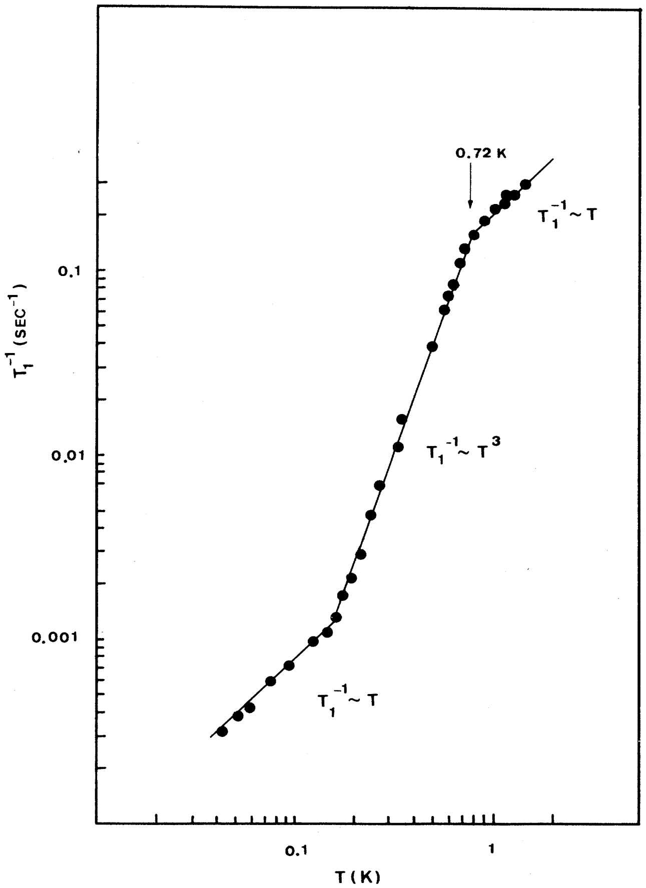


FIG. 1. The temperature dependence of spin-relaxation rates of $^9$Be in $UBe_{13}$.

property of $UBe_{13}$, and *if* the impurity contributing to the fluctuating nuclear local field follows a linear temperature dependence, the relaxation rate $1/T_1$ can be attributed to a combination of a $T^3$ power law and a relaxation contribution due to impurities.

$$1/T_1 = AT^3 + BT , \tag{24}$$

where $B$ is associated with the concentration of impurities. If $B \ll T$, then $1/T_1 \approx AT^3$ when 0.2 K $< T \ll T_c$. However, at very low temperatures, $AT^3$ becomes very small, so that the contribution to the relaxation rate from impurities begins to dominate. Thus, when $T < 0.16$ K, then $1/T_1 \simeq BT_1$. However, the impurity effect in this sample is unknown, and there is no reason to assume that the impurity contribution to the nuclear spin-lattice relaxation rate is proportional to temperature. The $T_1^{-1}(T)$ behavior below 0.2 K is still not clear. Below 0.1 K, the heating effect becomes a very serious problem. However, the relaxation times of $^9$Be in $UBe_{13}$ are very long at such low temperatures; for example, $T_1$ is 700 s at 0.1 K, and $\simeq 1600$ s at 65 mK. We can easily regulate the temperature within a $T_1/10$ time range, so that the temperature independence of $1/TT_1$ below 0.16 K is not likely to be caused by a heating effect. To confirm the absence of a heating effect, we reduced the power of the rf amplifier, such that the amplitude of the pulse sequence was decreased. The pulse heating effect should then be reduced. The constancy of $T_1$ at different values of the power of the rf amplifier rules out the heating effect.

For a conventional BCS-type superconductor,[16–19] $1/T_1$ exhibits a slight increase just below $T_c$ as a result of a piling up of the density of states at the gap edges, followed by an exponential decrease in the rate at lower temperature:

$$T_1^{-1} \propto \exp(-\Delta/k_B T) , \qquad (25)$$

where $2\Delta$ is the size of the energy gap. This dependence reflects the fact that electrons must be thermally excited across the gap to contribute to nuclear relaxation.[20] The apparent lack of enhanced behavior in the $T^{-1}(T)$ measurements just below $T_c$ suggests that the appreciable density of quasiparticle state exists in a low-energy region. One model which provides a low-lying excitation state in a straightforward manner is an energy-gap anisotropy. The theoretical densities $N_s(E)$ of superconducting quasiparticle excited state for $p$-wave triplets are given in Fig. 2.[21] In particular, as we had mentioned before, the polar-state model for $L=1$ triplet pairing can account for the observed $T^3$ behavior of $1/T_1$. More generally, if the superconducting gap function has lines of zero on the Fermi surface, $1/T_1$ will follow a $T^3$ power law.

The recent discovery of superconductivity at ambient pressure above 90 K in Y-Ba-Cu-O oxides[22] has given an impetus to a tremendous amount of experimental and theoretical research work. The superconducting phase has now been identified as $YBa_2Cu_3O_{7-\delta}$ (Ref. 23) with lattice parameters $a=3.82$ Å, $b=3.88$ Å, and $c=11.67$ Å. The structure[24] can be defined as two-dimensional slabs perpendicular to the $c$ axis separated by Y atoms. In each of these slabs the Cu sites have two coordinations [Cu(1) and Cu(2)], which differ in the configuration of the surrounding oxygens [Cu(1): planar next-nearest-neighbor–oxygen configuration]. The spin-relaxation rates of $^{63}Cu$ in $YBa_2Cu_3O_{7-\delta}$ at the Cu(1) site had been reported by Walstedt *et al.*,[25] Lippmaa *et al.*,[26] and Brinkmann.[27] The $^{63}Cu$ spin-lattice relaxation rate $1/T_1$ for the Cu(1) site is plotted versus $T$ and shown in Fig. 4. In this figure, the data above 77 K are taken from the work done by Walstedt *et al.*[25] because they only took measurements from room temperature to 77 K. Whereas when $T<77$ K, the data points are chosen from the work of Lippmaa *et al.*[26] At low temperatures, the $^{63}Cu$ spin-lattice relaxation process is nonexponential, particularly at near-helium temperatures.[26] It has at least one fast $T_{11}$ and one slow $T_{12}$ components[26] These data are anomalous in several ways. First, the spin-lattice relaxation rate is very flat with an apparent maximum just below room temperature, contrary to the expected Korringa behavior. The Cu(1) site relaxation in Fig. 3 shows no peak at $T_c$. This behavior is again in disagreement with the conventional BCS theory. Well below $T_c$, $1/T_1$ drops slightly. Similar property is also observed in $T_1^{-1}(T)$ of Be in $UBe_{13}$. Similar to the $T_1^{-1}(T)$ measurements of $^9Be$ in $UBe_{13}$, an apparent lack of enhanced behavior in the $T_1^{-1}(T)$ of $^{63}Cu$ in the $YBa_2Cu_3O_{7-\delta}$ suggests that there exists considerable low-energy density of states. If the low-energy density of states are not caused by pair breaking, one model which provides a low-lying excitation state in a straightforward manner is an energy-gap anisotropy. The nonexponential behavior of the $^{63}Cu$ spin-lattice relaxation process might be due to two different kinds of relaxation mechanisms in $^{63}Cu$ spin-lattice relaxation processes in $YBa_2Cu_3O_{7-\delta}$. As shown in Fig. 3, when 40 K $<T<T_c$, the fast spin-lattice relaxation rate $T_{11}^{-1}(T)$ is proportional to $\exp(-\Delta/k_B T)$ with $\Delta \simeq 130 k_B$ (the reported values of the gap energy $\Delta$ is 150 K by infrared reflectivity measurements[28] and is 206 K by tunneling measurements[29]). However, the slow relaxation rate $T_{12}^{-1}(T)$ is proportional to $T^3$ at the same temperature range. Therefore, the superconducting mechanism which causes the slow relaxation rate $T_{12}^{-1}(T)$ of $^{63}Cu$ in $YBa_2Cu_3O_{7-\delta}$ might be the same as that of $^9Be$ in $UBe_{13}$. The temperature dependence of the $^{63}Cu$ spin-lattice relaxation rate in $CeCu_2Si_2$ is quite similar to that of $^9Be$ in $UBe_{13}$. Hence, the superconducting mechanism in heavy-fermion superconductors might also take the responsibility for the superconductivity in high-$T_c$ superconductors. The $^{85}Y$ spin-lattice relaxation rate $T^{-1}(T)$ in $YBa_2Cu_3O_{7-\delta}$ has been reported by Markert *et al.*[30] Right below $T_c$, the relaxation rate drops only slightly below the Korringa value. Then, in a narrow temperature range between $1.1<T_c/T<1.2$, a rapid decrease in the relaxation rate is observed. Because the yttrium atoms in $YBa_2Cu_3O_{7-\delta}$ are not located in the presumed conducting plane, it is not expected to observe any phase transition in $^{89}Y$ $T_1^{-1}(T)$ measurements. Markert *et al.* claimed that the decrease of $T_1^{-1}(T)$, when $T<T_c$, might be due to a

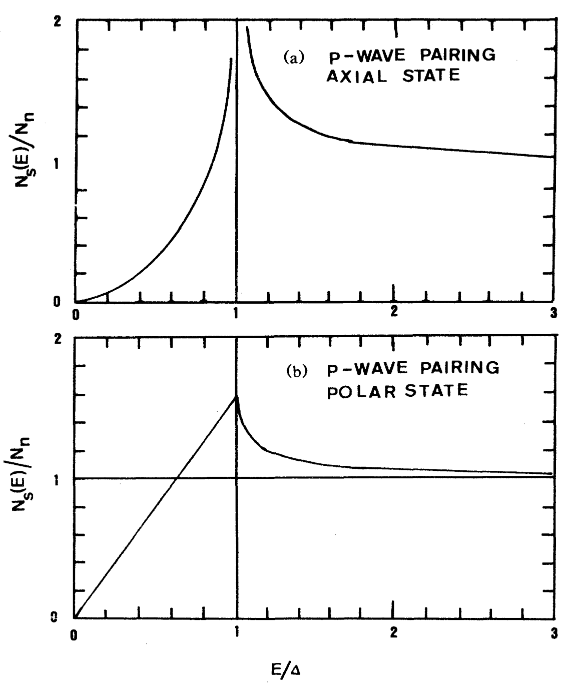


FIG. 2. Theoretical densities of superconducting quasiparticle excited states $N_s(E)$ for $p$-wave anisotropic superconducting pairing (a) axial (ABM) state $N_s(E)$ is proportional to $E^2$ for $E \ll \Delta$. (b) Polar state $N_s(E)$ is proportional to $E$ for $E \ll \Delta$.

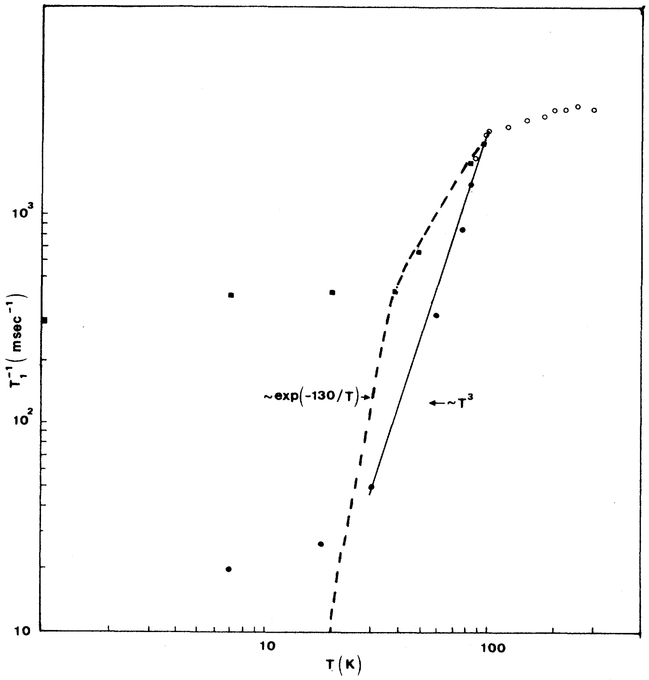


FIG. 3. The temperature dependence of spin-relaxation rates of $^{63}$Cu in $YBa_2Cu_3O_{7-\delta}$. (The open circles are taken from Ref. 25, the closed circles are the slow components of $1/T_1$ in Ref. 26, and the closed squares are the fast components of $1/T_1$ in Ref. 26.)

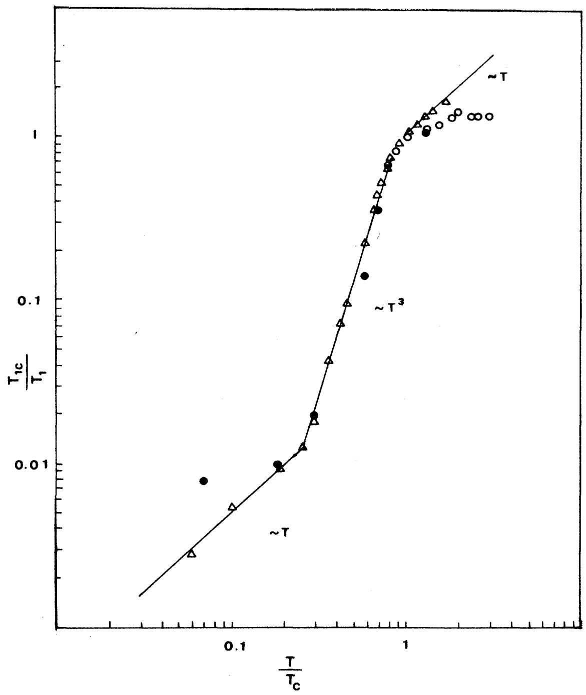


FIG. 4. The temperature dependence of spin-relaxation rates of $^9$Be in $UBe_{13}$ (triangles) are those of $^{63}$Cu (open circles are from Ref. 25 and closed circles are from Ref. 26) in $YBa_2Cu_3O_{7-\delta}$.

changing electronic structure. Such a change would presumably involve decreased conduction-electron wave-function density in the vicinity of yttrium atoms and an accompanying increase of electron density in the Cu—O chains or Cu—O planes would be necessitated by probability conservation. The interactions between $^{63}$Cu nuclei and two different sources of electrons (electrons which come from an yttrium atom and a Cu atom) would account for the two different relaxation rates of $^{63}$Cu in $YBa_2Cu_3O_{7-\delta}$. The behavior of $^{63}$Cu $T_1^{-1}(T)$ in $YBa_2Cu_3O_{7-\delta}$ at low temperature ($T < 30$ K) is not understood yet. If this behavior of $^{63}$Cu $T_1^{-1}(T)$ in $YBa_2Cu_3O_{7-\delta}$ is an intrinsic property of high-$T_c$ superconductors, the origin of this behavior is not yet known. However, a similar behavior is also found in $UBe_{13}$, a heavy-fermion superconductor. The observed temperature dependence of $T_1$ above $T_c$ indicates that $YBa_2Cu_3O_{7-\delta}$ is a poor metal. Indeed, it is well known that the normal-state dc electrical resistivity of $YBa_2Cu_3O_{7-\delta}$ is high[23] when $\rho \simeq 700$ $\mu\Omega$ cm at 300 K. Comparing the temperature dependence of the relaxation rate of high-$T_c$ superconductors with that of heavy-fermion superconductors, we plotted $T_{1s}/T_{1n}$ vs $T/T_c$ for the $UBe_{13}$ and $T_{11s}/T_{11n}$ vs $T/T_c$ for the $YBa_2Cu_3O_{7-\delta}$ as shown in Fig. 4, where $T_{11s}$ and $T_{11n}$ are the slow components of $^{63}$Cu spin-lattice relaxation times in $YBa_2Cu_3O_{7-\delta}$ at the superconducting state and normal state, respectively. As illustrated in Fig. 4, below $T_c$, these two kinds of materials demonstrate similar temperature dependence of the relaxation rates. It is suggested that the high-$T_c$ superconductors and the heavy-fermion superconductors have the same electron pairing mechanism. When $T > T_c$, the deviation of the spin-lattice relaxation rate of $^{63}$Cu in $YBa_2Cu_3O_{7-\delta}$ from the Korringa relation only indicates that $YBa_2Cu_3O_{7-\delta}$ is a poor metal.

A markedly increasing sound velocity of ultrasonic measurement about 200 K for $YBa_2Cu_3O_{7-\delta}$ had been observed.[31] A remarkable ultrasonic attenuation peak is also seen around 200 K, implying a tendency to some kind of lattice instability or structural phase transition.[32] Thermal analysis experiments were conducted to prove this idea.[32] Clear heat-flow anomalies can be seen in a differential scanning calorimetry curve for the $YBa_2Cu_3O_{7-\delta}$ sample. Clear evidence was also obtained from positron annihilation and TEM electron diffraction experiment. It is very significant that near 225 K the shape of the TEM electron diffraction spot changes. This change may be attributed to the changes of some ion equilibrium position.[32] Therefore, He *et al.*[32] claimed the existence of lattice instability or structural phase transition near 250 K. Zhang and co-workers[32] studied the x-ray-diffraction pattern around the strongest profile 130/101 and found that remarkable changes, occurring near 110 K, showed a tendency towards a structure of lower symmetry. However, with further cooling (to 78 K) the original high-symmetry (orthorhombic) phase is recovered. This would strongly suggest that the $YBa_2Cu_3O_{7-\delta}$ sample has a lattice instability before the superconducting phase transition. An anomalous $^{63}$Cu relaxation behavior in $YBa_2Cu_3O_{7-\delta}$ was also found between 200 and 240 K.[26]

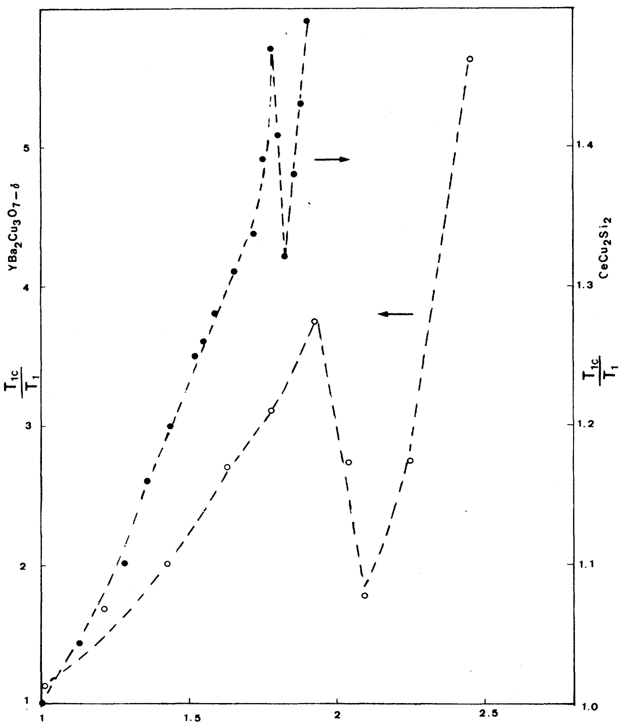


FIG. 5. The temperature dependence of $^{63}Cu$ spin-lattice relaxation times in $CeCu_2Si_2$ (closed circles) and $YBa_2Cu_3O_{7-\delta}$ (open circles) at normal states.

Since $T_c \simeq 98$ K, this anomalous peak happens at $T/T_c \simeq 2$. In $CeCu_2Si_2$, a similar but much smaller anomalous peak was observed[33] at 1.2 K; this temperature corresponds to $T/T_c \simeq 1.85$ as shown in Fig. 5. To confirm the anomaly of $T_1^{-1}(T)$ (which is much outside the error bars) at 1.2 K in $CeCu_2Si_2$, the $T_1$ measurement between 1.3 to 1.0 K was repeated at least 3 times. So this anomalous peak was unlikely to be an experimental artifact. We speculate that this feature is also due to either a structural phase transition or lattice instability. Further experiments, e.g., x-ray diffraction, would be helpful in elucidating this behavior. The relation between the structural phase transition and the superconducting mechanism is still not clear. However, Jorgensen, Hinks, and Felcher[34] studied the correlation between the structural transition and the superconducting transition and found that $PbMo_6S_8$ may never succeed to achieve a $T_c$ higher than 14 K unless the transition to lower symmetry (triclinic) phase can be suppressed.[32]

### III. THE TRANSVERSE RELAXATION TIME

The transverse (spin memory) relaxation rate $1/T_2$ is related to the fluctuation noise spectrum $J(\omega)$ of nuclear local-field fluctuations at $\omega = \omega_Q$ (where $\omega_Q$ is a Larmor precession frequency of a spin system), and $\omega = 0$. Transverse relaxation times are frequently measured by using a standard Hahn spin-echo technique. Usually the magnitude of spin-echo decays exponentially; $T_2$ is defined as

$$S(t) = S(0)\exp(-t/T_2) . \qquad (26)$$

When a sample enters a type-II superconducting state, in the intermediate region $H_{c2} > H_0 > H_{c1}$, the magnetic field penetrates into the superconductor in the form of fluxoids which arrange themselves in a two-dimensional periodic lattice. By the inhomogeneous magnetic field associated with the fluxoid structure, the resonant frequency of adjacent nuclear spin will be shifted. These frequency shifts can be large enough to inhibit mutual spin-flip processes.[7] When the average field gradient of the inhomogeneous magnetic field between nearest-neighbor nuclei is larger than the average local field at the site of a nucleus, due to the spin of one of its nearest neighbors, the fluxoid structure is sufficient to detune the spins and increase $T_2$. Usually when a material is in the superconducting state, the inhomogeneity in the magnetic field caused by the fluxoid structure should be sufficient to partially detune the spins. Consequently, just below $T_c$, $T_2$ increases as the temperature is decreased.

However, the transverse relaxation times of $^{89}Y$ in $YBa_2Cu_3O_{7-\delta}$ reported by Markert *et al.*[30] are quite unusual. The transverse relaxation was exponential and temperature independent in the normal state, with a decay-time constant $T_2 = 4.9 \pm 0.1$ ms. Below $T_c$, $T_2$ decreased with decreasing temperature and the decay became closer to Gaussian in shape. Therefore, the temperature dependence of $T_2$ in $YBa_2Cu_3O_{7-\delta}$ is quite unusual. Markert *et al.*[30] claimed that the temperature dependence of $^{89}Y$ might be due to spin diffusion. The relaxation processes, such as spin diffusion to normal vortex cores[35,36] and motion of the vortex lattice, would result in faster relaxation rates in the mixed state. Spin diffusion involves mutual spin flip between neighboring $^{89}Y$ nuclei; such transport will eventually equilibrate the slowly relaxing nuclei in the superconducting region with those in the more quickly relaxing normal-state vortex cores.[11]

For the heavy-fermion superconductor $UBe_{13}$, the transverse relaxation time $T_2$ of $^9Be$ in $UBe_{13}$ also exhibits the very unusual behavior like those of high-$T_c$ superconductor $YBa_2Cu_3O_{7-\delta}$. The transverse relaxation is close to exponential and temperature independent in the normal state. Below $T_c$, $T_2$ decreases with decreasing temperature and the decay becomes close to Gaussian in shape. The spin-echo peak of $^9Be$ magnetization, which is normalized to the value at spin-echo time 400 $\mu$s, is represented as a function of echo time for several temperatures in Fig. 6.

Since the decay process of spin-spin interaction in $UBe_{13}$ is approximately more Gaussian than exponential, the $T_2$ is defined as

$$S(t) = S(0)\exp(-t^2/2T_2^2) \qquad (27)$$

and the temperature dependence of $T_2$ in $UBe_{13}$ is shown in Fig. 7. Above the transition temperature $T_c \simeq 0.8$K, $T_2$ is a constant of temperature. However, a decrease of $T_2$ with decreasing temperature is observed below 0.8 K. There is either some property of the superconductivity reducing the detuning effect, or some additional relaxation

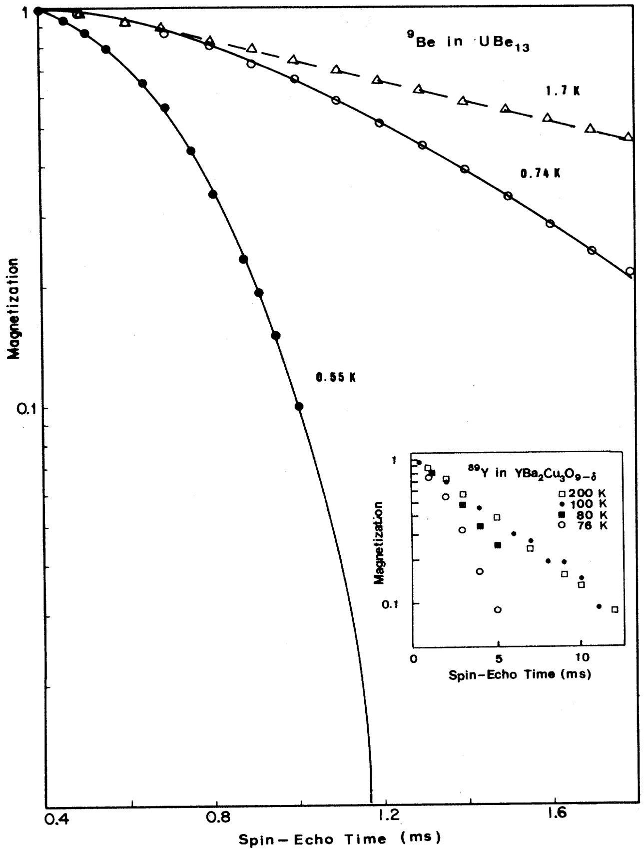


FIG. 6. Spin-echo peak of $^{9}Be$ in $UBe_{13}$ as a function of echo time for several temperatures. The inset shows the $^{89}Y$ magnetization in $YBa_2Cu_3O_{7-\delta}$ from Ref. 30.

process, such as spin diffusion, affecting $T_2$ below $T_c$. It might be due to some conduction-electron-mediated interactions which are stronger in the superconducting state than in the normal state. Usually the strength of the indirect interaction is less than one-tenth of the direct one,[37] and in particular, a strong indirect interaction is very unlikely between light atoms such as Be. The similarity of

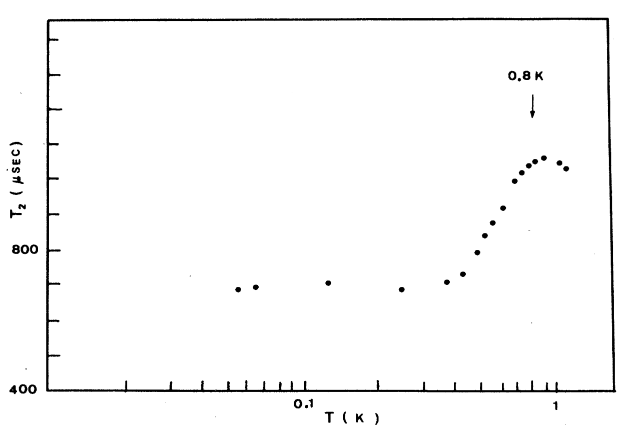


FIG. 7. The temperature dependence of $^{9}Be$ $T_2$ in $UBe_{13}$.

spin-spin relaxation behaviors in $UBe_{13}$ and $YBa_2Cu_3O_{7-\delta}$ are very obvious. Therefore, if the temperature dependence of $T_2$ is truly an intrinsic property of $UBe_{13}$, the nature of the spin-spin interaction in the superconducting state of $UBe_{13}$ is a very interesting problem, and it strongly suggests that the superconducting mechanisms in $UBe_{13}$ and $YBa_2Cu_3O_{7-\delta}$ are the same.

## IV. THE KNIGHT SHIFT IN THE SUPERCONDUCTING STATE

The magnetic resonance frequency $\omega_0$ is directly proportional to the applied magnetic field, $\mathbf{H}_0$. Since the electrons in the solid responding to $\mathbf{H}_0$ will cause an additional field $\Delta\mathbf{H}$ at the resonating nucleus, the nuclei in different environments will contact with different resonance fields.

**H** is often referred to as the local field. Therefore, the internal field **H** responsible for resonance in a material is

$$\mathbf{H}=\mathbf{H}_0+\Delta\mathbf{H}\,. \qquad (28)$$

At a fixed frequency $\omega_0$, by varying the applied magnetic field, one can map these internal fields by the NMR absorption line spectrum.

In general, the ratio of the total internal field and the local field $H$ is referred to as the Knight shift. The Knight shift $K$ is a gauge of the internal static field at the site of the probe nucleus,[38] and provides information on the coupling strength between nuclei and electronic spins.

For each term of the conduction-electron susceptibility there also exists a corresponding term in the Knight shift:

$$K=K_s+K_{\rm orb}+K_{ns}=\alpha\chi_s+\beta\chi_{\rm orb}+\gamma\chi_{ns}\,. \qquad (29)$$

Here $\chi_s$ is the $s$-band Pauli susceptibility, $\chi_{\rm orb}$ is the Van Vleck orbital susceptibility, and $\chi_{ns}$ represents the Pauli susceptibility of the non-$s$ bands, of which the $d$ band in transition metals[39] and the $f$ band in intermetallic compounds[40] will be particularly important.

The theory of the Knight shift in superconductors was derived by Yosida[41] from the BCS theory. Since all ground-state pairs in the superconducting state are either occupied or unoccupied, and hence contribute nothing to the spin susceptibility, only excited states need be considered. Because the occupation number of the excited states drops with decreasing temperature, the paramagnetic $s$-state spin susceptibility $\chi_s$ (and Knight shift $K_s$) should correspondingly decrease from its normal value below the transition temperature $T_c$ and vanish at $T=0$ K. The paramagnetic susceptibility $\chi_s$ in the superconducting state can be written as[41]

$$(\chi_s)_{sc}=(\chi_s)_n Y(T)\,, \qquad (30)$$

$$Y(T)=(\beta\Delta^{-1}d\Delta/d\beta)/(1+\Delta^{-1}d\Delta/d\beta)\,, \qquad (31)$$

where $2\Delta$ is the energy gap, $\beta=1/k_BT$, and $(\chi_s)_n$ is the susceptibility at normal state which can be obtained by setting $\Delta=0$ in $(\chi_s)_{sc}$.

The Van Vleck orbital susceptibility $\chi_{\rm orb}$ is due to currents produced by the "unquenching" of orbital angular momentum by the applied field. Therefore, $\chi_{\rm orb}$ is independent of the spin states of the conduction electrons, and so $K_{orb}$ will not be changed by spin pairing in the superconducting state.

Because $K_{ns}$ is proportional to the spin polarization of the non-$s$ band, its contribution to the Knight shift should disappear in the superconducting state if these non-$s$-band electrons participate in the formation of Cooper pairs.

There are two models used to predict the properties of triplet superconductivity in $^3$He. One is called the ABM or ESP model, first suggested by Anderson and Morel,[42] and the other is called the BW model, first suggested by Balian and Werthamer.[43] In the ESP (equal spin pairing) model, the appropriate superconducting state is a coupling of single-electron states of parallel spin components, $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$, thus allowing only electron pairs with spin component $S_Z=+1$. The contribution of the susceptibility of the spin-singlet BCS pairing, $|\uparrow\downarrow\rangle$ or $|\downarrow\uparrow\rangle$, vanishes due to antiparallel spins. This pairwise cancellation does not exist in ESP. Therefore, in the ESP model the Knight shift will not be changed by the electron pairing in the superconducting state. However, in the BW model the pairing states can be described as equal admixtures of $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $\frac{1}{2}(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle)$; as a result, one-third of the pairs are formed by spin-up and spin-down electron pairs, which will cause a cancellation of the susceptibility. Therefore,[40]

$$\chi_{sc}/\chi_n=\frac{2}{3}+\frac{1}{3}Y(T)\,, \tag{32}$$

with $Y(T)$ being the ratio calculated by Yosida for the BCS state, Eq. (31). The electron-electron interaction as described by Landau Fermi-liquid theory can alter $K(T)$. Clearly, one can obtain information about the nature of electron pairing in these superconductors by investigating the behavior of the Knight shifts in heavy-fermion superconductors and high-$T_c$ superconductors. However, we should note that these models are originally used to describe $^3$He, not heavy-fermion superconductors and high-$T_c$ superconductors which have lattice structure.[44,45] Additionally, the spin-orbital interaction in a superconducting pair, which has been neglected, might be important in the heavy-fermion superconductors.

The $^9$Be NMR absorption line spectra in the $UBe_{13}$ sample 2 from 0.9 to 0.061 K are shown in Fig. 8. These NMR spectra were obtained from traces of the integrated spin-echo intensity as a function of the swept field. These are typical quadrupole-split spectra of nuclear spin $\frac{3}{2}$, with a central $(\frac{1}{2}\rightarrow-\frac{1}{2})$ transition and unequally spaced quadrupole satellites. Since the sample we used to measure the spectra contains only a few single crystals, a symmetric powder pattern would not be expected. A curious property of these spectra is the absence of shifts or of the broadening of spectrum in the superconducting state. A shift and a broadening of spectrum should arise from the inhomogeneous flux expulsion which is characteristic of type-II mixed-state vortex lattice.[11] Apparently, since the $UBe_{13}$ spectra are essentially unchanged when the temperature falls just below the transition temperature $T_c=0.7$ K, there is little (or "no observed") variation of the magnetic field seen by the nuclei inside the sample. The absence of shifts in the NMR spectra taken above and below $T_c$ for $UBe_{13}$ is consistent with the suggestion

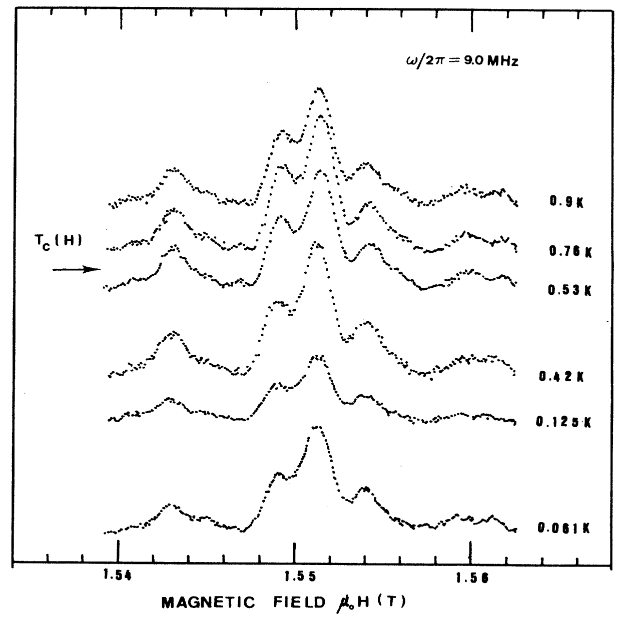


FIG. 8. NMR spectra $^9$Be in $UBe_{13}$, normal $T>T_c$ and superconducting state.

that $UBe_{13}$ belongs to the class of ABM $p$-wave superconductors in which Knight shifts in the superconducting state are the same as those just above $T_c$.

The $^{63}$Cu Knight-shift measurements of $YBa_2Cu_3O_{7-\delta}$ were carried out for Cu(1) and Cu(2) sites in crystallites oriented at right angle to a very strong magnetic field by Lippmaa *et al.*[26] The Knight shift of Cu(2) changes from the value in the normal state $K_n=0.56\%$ at $T\geq T_c$ to $K_s=0.30\%$ at $T=6$ K and does not approach zero as expected in the full pairing of the Bardeen-Cooper-Schrieffer theory. A similar general tendency is apparent for Cu(1) shifts as well. This behavior is consistent with

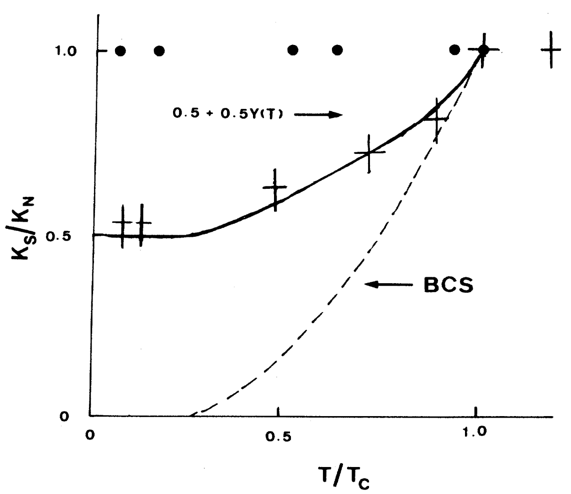


FIG. 9. The temperature dependence of Knight shift of $^9$Be (closed circles) in $UBe_{13}$ and those of $^{63}$Cu(2) in $YBa_2Cu_3O_{7-\delta}$ (crosses, Ref. 26).

the double-exponential $^{63}$Cu spin-lattice relaxation process, which suggests that the pairs in $YBa_2Cu_3O_{7-\delta}$ may be a combination of $s$- and $d$-state electron-electron pairs. If this argument is correct, the Knight shift of $^{63}$Cu in high-$T_c$ superconductors should be as follows:

$$K_s/K_n = A + BY(T) . \quad (33)$$

When temperature approaches 0 K, $K_s/K_n \simeq 0.5$. Therefore, $B$ is equal to 0.5. As shown in Fig. 9, the Knight shifts of Cu(2) can be fitted very well by choosing $A = 0.5$, which implies that the two electrons will form the $s$ state or $p$ state pair in superconducting state equally.

A similar temperature dependence of $^{63}$Cu Knight shift in $YBa_2Cu_3O_{7-\delta}$ is also reported by Kitaoka *et al.*[46]

## V. CONCLUSION

The features of magnetic resonance in high-$T_c$ superconductors are extremely similar to those of heavy-fermion superconductors. Therefore, it is quite possible that these two superconductors have the same pair mechanism. A rapid decrease in the relaxation rate of $^{89}$Y in $YBa_2Cu_3O_{7-\delta}$ is observed.[20] In a narrow temperature range between $1.1 < T_c/T < 1.2$, this decrease of about a factor of 3 over a 10-K range in much greater than is expected. This behavior indicates that the conduction electrons in the vicinity of the yttrium atoms, at superconducting transition temperature $T_c$, will move to the Cu–O plane, such that the electron density in the Cu–O plane becomes extremely high. Because of the high density of the electron gas and the short coherent length at high temperature, the strong Coulomb repulsion will prevent the conduction electrons from forming the conventional BCS electron pairs. The same kind of situation also happens in heavy-fermion superconductors. In heavy-fermion superconductors, the range in frequency of the Coulomb repulsion between electrons is similar to that of the phonon-induced attraction and therefore, no net attraction is in the $s$-wave channel.[47] If the pair wave function has a node at the origin, as in finite angular momentum pairing, the short-range part of the repulsion is not felt. A pairing mechanism which can overbear the Coulomb repulsion between electrons with a very high density of conduction electrons in a local area (e.g., a two-dimensional surface) might be the source of high superconducting transition temperature in the new copper oxide superconductors.

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