Effect of impurity resonance states on the NMR spectra of high-$T_c$ cuprates

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A strong nonmagnetic impurity can induce a resonance state in the $d$-wave superconducting state. As far as magnetic properties are concerned, this resonance state behaves effectively like a free moment. It leads to a Curie-Weiss-like magnetic susceptibility in an intermediate temperature regime below $T_c$. From the impurity susceptibility, the effective moment of the resonance state is deduced and compared with experiments. The contribution of the resonance to the magnetic susceptibility can account for the main feature of the NMR spectra in overdoped high-$T_c$ materials. In the underdoped regime, the contribution from the resonance to the magnetic susceptibility is also substantial, but the effective moment of the resonance is smaller than the total moment induced by a nonmagnetic impurity.

The substitution of impurities into cuprates has served as an important probe in the study of high-temperature superconductivity. Experiments were performed with magnetic (Ni) as well as nonmagnetic (Zn, Li, Al) impurities. Ni$^{2+}$ carries a local moment. It leads to naturally some kind of Kondo physics. However, the behavior of nonmagnetic impurities is surprising. Theoretical analysis indicates that Zn or some other nonmagnetic impurities in CuO$_2$ planes is a strong potential scatterer. It can induce a sharp resonance peak near the Fermi level in a $d$-wave superconducting state. This low-energy resonance peak was observed in the scanning tunneling spectroscopy (STM) measurement around a Zn impurity and the STM pattern associated can be understood by considering the effect of tunneling filter.

However, the interpretation to the experimental data obtained from magnetic measurements is still controversial. A series of nuclear magnetic resonance (NMR) experiments, such as the $^{89}$Y NMR width of YBa$_2$(Cu$_{1-x}$Zn$_x$)$_2$O$_y$ samples with $x > 0.5$ showed that the magnetic susceptibility associated with Zn or other nonmagnetic impurities exhibits a Curie-like behavior. This led to the suggestion that some uncompensated spins are induced by Zn in a correlated background with strongly antiferromagnetic fluctuations. However, muon spin resonance ($\mu$SR) measurements on a number of YBa$_2$(Cu$_{1-x}$Zn$_x$)$_2$O$_y$ samples with different Zn content found no evidence for an additional local moment induced by Zn above the background. It was suggested that the Curie-like Knight shift observed in NMR experiments may result from a sharp low-energy peak in the density of states already observed by STM, rather than from induced local moments. In the overdoped regime, since the magnetic correlation is dramatically suppressed, the formation of induced local moments has also been questioned.

In this paper, we investigate the effect of resonance states induced by a strong nonmagnetic impurity on NMR spectra in a $d$-wave superconducting state. The contribution of the resonance state to the spin-lattice relaxation rate as well as the Knight shift is shown to be Curie-Weiss-like. From the impurity susceptibility, the effective moment of the resonance state is determined and compared with experiments. Our result is obtained in the superconducting state. We believe that it can be also qualitatively applied to the pseudogap phase of high-$T_c$ oxides, since the normal state pseudogap has similar symmetry as the $d$-wave superconducting gap.

Let us consider the following BCS mean-field Hamiltonian of $d$-wave superconductors with a nonmagnetic impurity.

$$H = \sum_k C^\dagger_k (\xi_k \tau_3 - \Delta_k \tau_1) C_k + \frac{V}{N} \sum_{k,k'} C^\dagger_{k'} \tau_3 C_{k'},$$

where $C^\dagger_k = (c^\dagger_{k\uparrow}, c_{-k\downarrow})$ and $\xi_k$ is the energy dispersion of normal electrons. $\tau_1$ and $\tau_3$ are the Pauli matrices. $\Delta_k = \Delta(T) \cos(2\phi_k)$ is the temperature-dependent gap function of $d$-wave superconductors and $\phi_k = \tan^{-1} k_y/k_x$. $V$ is the impurity scattering potential at $r = 0$.

For the $\delta$-function scattering potential defined in Eq. (1), only the $s$-wave scattering channel has a contribution to the scattering matrix. In this case, the Green’s function of electron can be rigorously expressed as

$$G(r, r', \omega) = G^0(r-r', \omega) + G^0(r, \omega) T(\omega) G^0(-r', \omega),$$

where $G^0(r, \omega)$ is the unperturbed propagator, which can be obtained from the Fourier transformation of the Green’s function $G^0(k, \omega)$ in the momentum space

$$G^0(k, \omega) = \frac{1}{\omega - \xi_k \tau_3 - \Delta_k \tau_1}.$$

For a $d$-wave superconductor, the $T$ matrix $T(\omega)$ is diagonal and determined by the following equations

$$T(\omega) = T_0(\omega) \tau_0 + T_3(\omega) \tau_3,$$

$$T_0 = \frac{G_0(\omega)}{\pi N_F c^2 - G_0(\omega)^2},$$

$$T_3 = \frac{c}{\pi N_F c^2 - G_0(\omega)^2}.$$
where \( N_F \) is the normal density of states at the Fermi level and
\[
G_0(\omega) = \frac{1}{\pi N_F} \sum_k \frac{\omega}{\omega^2 - \xi_k^2 - \Delta_k^2},
\]
c = \cot \delta_0 = 1/(\pi N_F V) \text{ and } \delta_0 \text{ is the scattering phase shift. In the strong scattering (or unitary) limit } \delta_0 \sim \pi/2 \text{ and } c \sim 0. \text{ In the weak scattering (Born) limit, } \delta_0 \rightarrow 0 \text{ and } c \rightarrow \infty. \text{ In the discussion below, only the unitary scattering limit will be considered.}

In the complex \( \omega \) plane, \( T(\omega) \) has two poles when the condition \( G_0(\omega) = \pm c \) is satisfied. These two poles define the resonant states induced by an impurity and are present at
\[
\Omega_\pm = \Omega' \pm i\Omega'',
\]
where \( \Omega' \) denotes the resonance energy and \( \Omega'' \) the resonance peak width. For a Zn impurity, \( \delta_0 \approx 0.48\pi \) and \( c \approx 0.0629 \), both \( \Omega' \) and \( \Omega'' \) are found to be much smaller than the superconducting gap, \( (\Omega', \Omega'') \ll \Delta \). Thus a sharp resonance state is induced by a Zn impurity.

In the low-energy limit, the unperturbed Green’s function \( G^0(r, \omega) \) changes smoothly with \( \omega \) and \( \text{Im}G^0(\omega, \omega) \) approaches zero in the limit \( \omega \rightarrow 0 \). This means that the imaginary part of \( G^0(\omega, \Omega'') \) at the resonance energy is much smaller than its real counterpart and can be approximately taken as zero once \( r \neq 0 \). In this case, the impurity correction to the Green’s function is then approximately given by
\[
\delta G(r, r' \omega) \approx \text{Re}G^0(r, 0) T(\omega) \text{Re}G^0(-r', 0).
\]

The NMR spin-lattice relaxation and Knight shift are proportional to the imaginary and real parts of the magnetic susceptibility, respectively. To study the impurity corrections to these quantities, we use the Hamiltonian first proposed by Mila and Rice for the hyperfine interaction between nuclear spins and conduction electrons. This Hamiltonian contains direct hyperfine interactions as well as exchange-induced hyperfine interactions between neighboring sites. The spin-lattice relaxation rate at site \( r \) is then given by
\[
\frac{1}{T_1(r)T} = \frac{k_B}{4\mu_B^2 h^2} \sum_{j,l} F_{j,r} F_{l,r} \lim_{\omega \rightarrow 0} \frac{\chi''(j, l, \omega)}{\omega},
\]
where \( j \) or \( l \) runs over \( r \) and its four nearest neighbors. When \( j = r, F_{j,r} = A \) is the direct hyperfine coupling constant between the nuclei and the electrons on the same site. When \( j \neq r, F_{j,r} = B \) is the hyperfine coupling induced by the exchange interaction of Cu spins on the two nearest neighboring sites.

In the limit \( \omega \rightarrow 0 \), the magnetic susceptibility \( \chi''(j, l, \omega) \) is given by
\[
\lim_{\omega \rightarrow 0} \frac{\chi''(j, l, \omega)}{\omega} = \frac{\mu_B^2 \beta}{4\pi} \int_{-\infty}^{\infty} \frac{d\varepsilon}{\cosh^2(\beta\varepsilon/2)} A(j, l, \varepsilon),
\]
where
\[
A(j, l, \varepsilon) = [\text{Im}G_{11}(j, j', \varepsilon)]^2 + [\text{Im}G_{12}(j, j', \varepsilon)]^2,
\]
and \( \beta = 1/k_B T \). In the clean limit, \( V = 0, A(j, j', \varepsilon) \sim \varepsilon^2 \) in the low-energy limit \( \varepsilon \ll \Delta \). It can be readily shown from Eq. 6 that \( 1/T_1 \sim T^3 \). This \( T^3 \) behavior of \( 1/T_1 \) was observed in high-\( T_c \) cuprates, in support of d-wave superconductivity.

At low temperatures, the spin-lattice relaxation rate is mainly determined by the resonance state. Using Eq. 4 and assuming particle-hole symmetry, it is straightforward to show that the contribution of the resonance state to the spin-lattice relaxation rate is approximately given by
\[
\delta [T_1(r)T]^{-1} \sim \frac{k_B}{2\pi^2 h^2} \int_{-\infty}^{\infty} \frac{d\varepsilon}{\pi} [T_{11}''(\varepsilon)]^2 P(\varepsilon, T),
\]
where
\[
Z(r) = \sum_j F_{j,r} \left\{ [\text{Re}G^0_{11}(j, 0)]^2 + [\text{Re}G^0_{12}(j, 0)]^2 \right\},
\]
\[
P(\varepsilon, T) = \frac{1}{4k_B T \cosh^2(\varepsilon/2k_B T)}.
\]
In the intermediate-temperature regime, \( k_B T_c \gg k_B T \gg \Omega' \), the integration in Eq. 7 is contributed mainly from the pole of \( T_{11}(\varepsilon) \), thus one can replace approximately \( P(\varepsilon, T) \) by \( P(\Omega', T) \). In this case, \( P(\Omega', T) \sim 1/T \), and
\[
\delta [T_1(r)T]^{-1} \sim \frac{1}{T}.
\]
This \( 1/T \) behavior of \( (T_1 T)^{-1} \) was observed in Zn-substituted \( \text{YBa}_2\text{Cu}_4\text{O}_8 \) samples in the superconducting state.\( ^{22} \) It is also consistent with the \( 63\text{Cu} \) NMR data for Zn-substituted \( \text{YBa}_2\text{Cu}_3\text{O}_6.7 \).

In the low-temperature limit, \( k_B T \ll \Omega' \), since \( P(T) \) drops to zero exponentially with decreasing temperature, the impurity correction to the spin-lattice relaxation rate is exponentially small and negligible. In the NMR experiments, the fast drop of \( (T_1 T)^{-1} \) was generally taken as an indication of spin freezing.\( ^{38} \) However, the drop here is due to the fact that the resonance state has a finite excitation energy above the Fermi level and is difficult to be excited when \( k_B T \ll \Omega' \).

Thus \( \delta [T_1(r)T]^{-1} \) varies nonmonotonically with temperature. It first increases with decreasing temperature and then drops after reaching a maximum. In the unitary scattering limit, the peak temperature \( T_f \) of \( \delta [T_1(r)T]^{-1} \) is approximately given by \( k_B T_f \approx 0.65\Omega' \). For Zn-substituted materials, the induced resonance state energy \( \Omega' \sim 17 \text{ K} \).\( ^{17} \) The corresponding peak temperature is estimated to be \( T_f \sim 11 \text{ K} \), in agreement with the experimental data for \( \text{YBa}_2\text{Cu}_3\text{O}_{6.7}(\text{YBCO}) \) where the peak of \( (T_1 T)^{-1} \) is located at \( \sim 10 \text{ K} \).

Figure 1 shows the temperature dependence of \( \delta(1/T_1 T) \), normalized by the total spin-lattice relaxation.
rate \( N(T) = (T_1 T)^{-1} \) at \( T_c \), on one of the four nearest neighbors of the impurity. In obtaining the curves shown in this figure, the energy dispersion \( \varepsilon_k \) defined in Ref. 22 and the zero-temperature superconducting gap \( \Delta(0 \text{ K}) = 25 \text{ meV} \) are used. In this case, the normal state density of states \( N_F \) is about 1.9 eV\(^{-1}\). The results show that the impurity correction to the spin-lattice relaxation rate is very sensitive to the value of the phase shift \( \delta \). In the limit \( \delta = \pi / 2 \), \( (T_1 T)^{-1} \) increases monotonically with decreasing temperature.

The Knight shift is another important quantity measured by NMR experiments. It is determined by the real part of the static magnetic susceptibility \( \chi' \) (Ref 22),

\[
K(r) = \frac{1}{\gamma_e \hbar^2} \sum_j F_{jr} \chi'(j),
\]

where

\[
\chi'(j) = -\frac{\mu_B^2}{\pi} \int d\varepsilon P(\varepsilon, T) \text{Tr} \text{Im}\mathcal{G}(j, j, \varepsilon),
\]

In the unitary limit, \((\Omega', \Omega'') \ll \Delta\), the contribution from the resonance to \( \chi' \) is approximately given by

\[
\delta \chi'(j) \approx -\frac{\mu_B^2}{\pi} \text{Tr} \text{Re}\mathcal{G}^0(j, 0) \text{Re}\mathcal{G}^0(j, 0) \int d\varepsilon T^0_{11}(\varepsilon) P(\varepsilon, T).
\]

As for \( \chi'' \), the temperature dependence of \( \delta \chi'(j) \) is predominantly determined by the resonance pole; thus

\[
\delta \chi'(j) \sim P(\Omega', T).
\]

Again, in the intermediate-temperature regime \( k_B T_c \gg k_B T \gg \Omega', P(\Omega', T) \sim 1/T \), from Eq. (9) we then have

\[
\delta K(r) \sim \frac{1}{T}.
\]

Thus the resonance state lead to a Curie-like term in the Knight shift. In the low-temperature limit, \( k_B T \ll \Omega' \), \( P(\Omega', T) \) drops exponentially with temperature. This suppresses the divergence of \( K(T) \) in low temperatures and \( K(T) \) becomes zero at zero temperature. This is different from the behavior of a free local moment. The overall temperature dependence of the impurity contribution to the Knight shift \( \delta K(r) \) on one of the nearest-neighboring sites of the impurity is shown in Fig. 2. On other sites, for example, on one of the Y sites closest to an impurity in YBCO, the impurity correction to \( \delta K(r) \) is smaller but the overall temperature dependence behaves similarly.

The above results indicate that the impurity contribution to the Knight shift follows the Curie law in a broad temperature regime in the superconducting state. Thus the resonance state induced by an impurity is equivalent to a local magnetic moment in the magnetic measurement. This suggests that an effective moment corresponding to a resonance state can be defined from the magnetic susceptibility by the following equation,

\[
\frac{\mu_{\text{eff}}^2}{3k_B T} = \sum_j \delta \chi'(j),
\]

where the summation runs over the four nearest neighbors of the impurity. This effective moment can be used to characterize a nonmagnetic resonance state in the analysis of Knight shift data.

Figure 3 shows the effective moment \( \mu_{\text{eff}} \) corresponding to the resonance state. It should be emphasized that both \( \delta \chi' \) and the effective moments depend on the energy dispersion of normal electrons. The value of effective moment can be altered if an energy dispersion other than that given by Norman et al. is used. In particular, \( \delta \chi' \) is proportional to the normal state density of states \( N_F \). If \( N_F \) is doubled, then \( \mu_{\text{eff}} \) will increase by a factor \( \sqrt{2} \). Close to \( T_c \) or at very low temperatures, the effective moment of the resonance state becomes small and approaches zero in the zero-temperature limit. This is different from a free magnetic moment and can in principle be used to separate the contribution of the resonance state from that of a free magnetic moment.
If the temperature is not too low or too close to the critical temperature, the effective moment is about $0.3\mu_B$. This is close to the effective moment induced by Zn for slightly overdoped YBCO deduced from the magnetic susceptibility data. However, it is much smaller than the effective moment induced by Zn for underdoped YBCO or by Li for optimal doped YBCO. This indicates that the resonance state induced by a strong nonmagnetic impurity has substantial contribution to the NMR spectra in the high-$T_c$ superconducting state. This contribution should be taken into account in the analysis of the NMR data. However, the effective moment of the resonance state is smaller than the total moments induced by a nonmagnetic impurity in the underdoped regime. The difference between the total moment determined from magnetic measurements and the effective moment of the resonance state can be attributed to the contribution of local spins induced by a nonmagnetic impurity.

In conclusion, we have studied the effect of nonmagnetic impurities on the NMR spectra of high-$T_c$ superconductors. The resonance state near the Fermi surface induced by a unitary impurity behaves effectively like a magnetic moment in the $d$-wave superconducting state. It contributes a Curie-Weiss term to the NMR spin-lattice relaxation rate as well as the Knight shift in the temperature regime $\Omega' \ll k_BT \ll k_BT_c$. The contribution of this induced resonance state can account for the main feature of the NMR spectra in the superconducting state in overdoped high-$T_c$ materials. In the underdoped regime, the contribution of the resonance state to the NMR spectra is also substantial, but the effective moment of the resonance state is smaller than the total moments induced by a nonmagnetic impurity.

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