# Transition from strong to weak coupling with decreasing $T_c$ in the $Tl_2Ba_2CuO_{6+x}$ system

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The effect of an increase in the oxygen content on the parameters of the electronic system in the normal and superconducting states has been studied in oriented samples of the high-$T_c$ system $Tl_2Ba_2CuO_{6+x}$ with $T_c$'s from 115 to 30 K (with $x$ from 0 to 0.3). The study was carried out by an NMR method using $^{205}Tl$. The superconducting gap is found from the temperature dependence of the rate of spin–lattice relaxation and from the Knight shift of $^{205}Tl$. The ratio $\Delta/T_c$ decreases with decreasing $T_c$. This behavior indicates a corresponding weakening of the coupling upon doping with oxygen.

**1.** The $Tl_2Ba_2CuO_{6+x}$ system is distinguished from other high-$T_c$ superconductors in that the transition temperature $T_c$ can be varied by varying the oxygen content over a short interval, while the material remains in the same crystalline phase.[1,2] It thus becomes possible to study correlations between changes in transition temperature and changes in other parameters of the electronic system. In this letter we are reporting a decrease in the ratio $\Delta/T_c$, from 2.8 to 1.3, as $T_c$ is lowered from 115 to 30 K by a change in $x$ from 0 to 0.3. This behavior is evidence that there is a transition from strong coupling to weak coupling as the transition temperature is lowered in the $Tl_2Ba_2CuO_{6+x}$ system.

**2.** The size of the superconducting gap was determined from the temperature dependence of the rate of spin–lattice relaxation and the Knight shift of $^{205}Tl$ in $Tl_2Ba_2CuO_{6+x}$ samples with $T_c = 30$, 100, and 115 K at $T < T_c$. The external field was directed along the $(ab)$ crystallographic plane. As we reported in a previous paper[3] on $Tl_2$ $Ba_2CuO_{6+x}$ single crystals, the strong Meissner effect complicates efforts to analyze the temperature dependence of the shift of an NMR line when the field is applied along the $c$ axis. The Meissner effect is superimposed on the natural freezing of the Knight shift at $T < T_c$. Another complicating factor is the presence of a significant relative amount of normal phase in the cores of vortices. In the $H \| (ab)$ orientation these effects are less obvious because of the smaller value of $H_{c1}$ and the smaller core. In a study of single-crystal samples in this orientation, however, it turned out to be difficult to carry out measurements at temperatures $T < T_c$ because of the pronounced weakening of the signal, apparently due to a strong skin effect. The net result was that reliable data could be found only for the single crystal with $T_c = 115$ K in Ref. 3 in this range $[H \| (ab),\ T < T_c]$.

The test samples in the present study were ground $Tl_2Ba_2CuO_{6+x}$ single crystals with $T_c = 30$ and 100 K, mixed with Stycast 1266 epoxy resin and oriented in a field of 7 T. We used data from Ref. 3 on the single crystal with $T_c = 115$ K; the procedure for growing the crystals was also described in that earlier paper. As was shown in Ref. 2, the value $x = 0$ corresponds to a crystal with $T_c = 115$ K, while $x = 0.3$ corresponds to

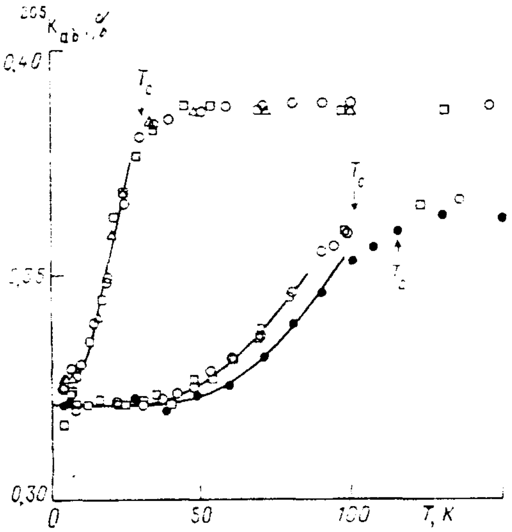

FIG. 1. Temperature dependence of the Knight shift ($K_{ab}$) of $^{205}$Tl in the orientation $H \| (ab)$. Open symbols: Oriented powdered samples ($T_c = 30$ and 100 K) in fields of 1.78 T (△), 3.58 T (□), and 7.05 T (○). ●—Single crystal with $T_c = 115$ K in a field of 7.05 T. The solid curves are approximations by the formula $K_{ab} = K_{ab}^L + \alpha \exp(-\Delta/T)$ with the values $\Delta/T_c = 1.4$, 2.3, and 2.6 (in order of increasing $T_c$).

$T_c = 30$ K. We used a Bruker MSL-300 pulsed NMR spectrometer, carrying out the measurements by the standard spin-echo and saturation–restoration techniques. The typical lengths of the 90° pulse were 1.3–1.7 μs. The measurements at $T < T_c$ were carried out in the field-cooling regime.

3. Figure 1 shows the temperature dependence of the Knight shift $K_{ab}$ for three test samples, measured in fields of 1.78, 3.58, and 7.05 T. At $T > T_c$ the Knight shift is independent of the temperature. When the sample is cooled below $T_c$, the Knight shift decreases rapidly. We see in Fig. 1 that the behavior of $K_{ab}$ at $T < T_c$ does not depend on the strength of the applied magnetic field. This independence shows (first) that the change in the NMR frequency upon the transition to the superconducting state is not due to a Meissner expulsion, and that the decrease in $K_{ab}$ results from a decrease in the density of states at the Fermi surface.[4] Second, it follows that the relative amount of superconducting phase present (due to the presence of vortices) in the superconducting state is negligible; otherwise we would see a shift of the line linear in the field as $T \to 0$ (and this shift would be quite different for samples with different $T_c$'s). We should therefore assume that the residual value $K_{ab}(T = 4.2\text{ K}) \simeq 0.323\%$ is a temperature-independent orbital part of the Knight shift, $K_{ab}^L$, which is the same (within the experimental errors) for all the test samples.

At $T > T_c$ the spin part of the Knight shift, $K^s$, calculated from $K_{ab}^L = K_{ab}(4.2\text{ K})$, increases, by a factor $\simeq 1.7$, as $T_c$ decreases from 115 to 30 K. This increase implies a corresponding increase in the density of electron states as the material is doped with oxygen. At $T < T_c$, the experimental points are described well by the formula $K_{ab} = K_{ab}^L + \alpha \exp(-\Delta/T)$, which reflects the freezing of $K^s$ upon the transition to the superconducting state.[4] The value found for $\Delta/T_c$ as a result decreases with decreasing $T_c$: $\Delta/T_c = 2.6$ ($T_c = 115$ K), 2.3 (100 K), and 1.4 (30 K).

We see in Fig. 1 that the residual shift $K_{ab}(4.2\text{ K})$ for the sample with $T_c = 30$ K is

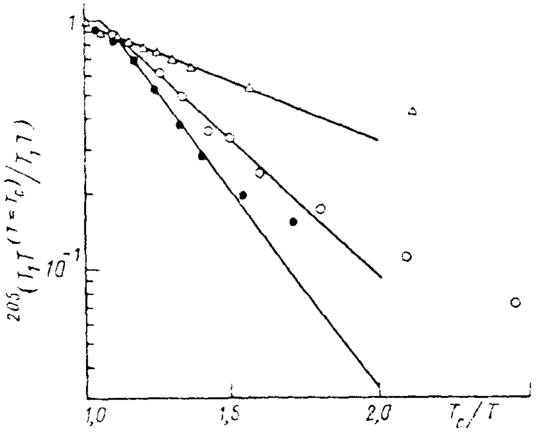

FIG. 2. The normalized product $^{205}(T_1T)^{-1}$ versus the normalized reciprocal temperature in a field of 7.05 T[$H \| (ab)$]. △,○,● — — — $T_c=30$, 100, and 115 K. The solid curves are approximations by the formula $(T_1T)^{-1} \propto \exp(-\Delta/T)$ with the values $\Delta/T_c = 1.1$, 2.5, and 3.0 (in order of increasing $T_c$).

slightly larger than for the two other samples. In principle, a nonzero residual shift can arise in the case of a pairing with an order parameter which is not of the *s* type, because of a zero superconducting gap at the Fermi surface. Since the spin part of the Knight shift for the 30-K sample is larger, this sample would also have a larger $K^s$ in the limit $T \rightarrow 0$. However, the difference between the values of $K_{ab}(4.2\ \mathrm{K})$ for the different samples lies right at the limit of the experimental accuracy. Our data thus cannot support any definite conclusion about a deviation of the symmetry of the order parameter from an *s* type.

**4.** Figure 2 shows, in semilogarithmic scale, the quantity $(T_1T)_{T=T_c}/(T_1T)$, where $T_1^{-1}$ is the rate of spin–lattice relaxation of $^{205}$Tl, as a function of the reciprocal temperature $T_c/T$. As was reported previously,[3] in the normal state the samples with the different $T_c$ 's do not exhibit any fundamental differences in the behavior of $T_1^{-1}$. Below $T_c$, in the interval $T_c > T > T_c/2$, the relaxation rate has a gap behavior, of the type[5] $(T_1T)^{-1} \propto \exp(-\Delta/T)$, as can be seen from Fig. 2. The values of $\Delta/T_c$ found by approximating these regions with this formula are 3.0, 2.5, and 1.1 for the samples with $T_c = 115$, 100, and 30 K, respectively. These values differ somewhat from the values of $\Delta/T_c$ found from the temperature dependence of the Knight shift (Fig. 1). The probable reason for this difference is the error of the simple formulas used in the approximation.

At $T < T_c/2$, the behavior of $T_1^{-1}$ deviates from exponential (Fig. 2). The apparent reason is an effect of other relaxation mechanisms. This possibility is supported by measurements[6] of the field dependence of $T_1^{-1}$. A more detailed analysis of the behavior of $T_1^{-1}$ in this region was published in Ref. 7.

**5.** Papers reporting measurements of the width of the superconducting gap by various methods on all possible high-$T_c$ superconducting samples,[8] including $\mathrm{YBa_2Cu_3O_x}$ with $6 < x < 7$ (Ref. 9), have usually reported values of $\Delta/T_c = 2.5$–$3.5$, without any noticeable correlation between this quantity and $T_c$. Our results show that in the overdoped $\mathrm{Tl_2Ba_2CuO_{6+x}}$ system the increase in the number of carriers due to an increase in the oxygen content leads to a decrease in not only $T_c$, but also the ratio $\Delta/T_c$. This result may be taken as evidence of a transition from a regime of strong coupling to one of weak

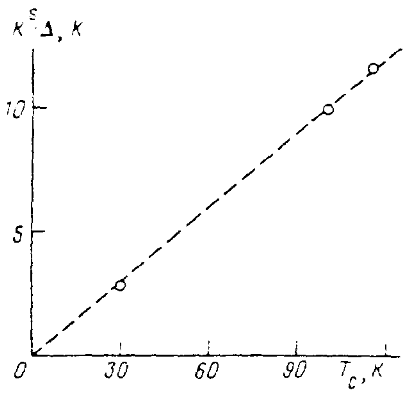

FIG. 3. Product of the spin part of the Knight shift, $K^s$, and the gap width $\Delta$ versus $T_c$.

coupling, in a given compound. If we assume a phonon pairing mechanism and use the expression[10]

$$\Delta/T_c = 1.76\{1+5.3(T_c/\Omega)^2\ln(\Omega/T_c)\},$$

where $\Omega$ is a characteristic frequency of the phonon spectrum, we find the value $\Omega = 320$ K for an approximation of the measured values of $\Delta/T_c$. From the equation[11]

$$T_c = 0.25\Omega\{\exp(2/\lambda)-1\}^{-1/2},$$

which relates $T_c$ to the electron–phonon coupling constant $\lambda$, we thus find values $\lambda = 0.96$, 4, and 5 for $T_c = 30$, 100, and 115 K.

Our results are also consistent with calculations carried out in Ref. 12 for underdoped $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 40$ K) and $YBa_2Cu_3O_{6.63}$ ($T_c = 60$ K) and also for $YBa_2Cu_3O_7$ ($T_c = 95$ K). Using a model of pairing through antiferromagnetic fluctuations, Monthoux *et al.*.[12] showed that an increase in the degree of doping leads to a decrease in the ratio $\Delta/T_c$ (from 4.3 for LSCO to 2.9 for $YBa_2Cu_3O_7$), while the coupling constant increases with $T_c$.

Another curious point is the $T_c$ dependence of the product of the spin part of the Knight shift and the width of the superconducting gap, $K^s\Delta$ (Fig. 3). We see that the relation $K^s\Delta \propto T_c$ holds quite well.

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