Interlayer Coupling in the Superconducting State of Bi2223

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Spin echo double resonance has been used to detect the spin–spin coupling between Cu spins on adjacent CuO_2 layers. These measurements, performed in the superconducting state, on the three layer Pb–doped bismuth high–T_c compound demonstrate the existence of interlayer exchange coupling as well as interlayer correlations in the quasiparticle excitations. An estimate of the interlayer exchange constant $J_\perp$ is found to be 43 K, 3% of the intralayer value.

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Antiferromagnetic correlations play a dominant role in the normal state properties of the cuprate superconductors. Intralayer coupling between moments on the Cu sites of the ubiquitous CuO_2 layers have been observed by several different techniques: inelastic neutron scattering[1], light scattering[2] and NMR[3]. The exchange constant $J_{||}$ between Cu moments is about 1500 K in magnitude. This is the same exchange constant used for example in t–J models to describe the strongly correlated nature of holes in a CuO_2 layer. Recently attention has focussed on the three dimensional nature of the cuprates, in particular to interlayer coupling. In addition to the intralayer coupling in high–T_c superconductors there is a weaker interlayer coupling. In the superconducting state for example the highly anisotropic compounds can be thought of as a superlattice of Josephson coupled layers. It is then natural to ask whether the magnetic coupling $J_{||}$ found within the CuO_2 layers has its interlayer analogue $J_\perp$. This interlayer coupling was first observed with inelastic neutron scattering[4,5] in YBCO. Oscillations in the scattering intensity along momentum transfer $(00l + \xi)$ are consistent with coupling between the adjacent CuO_2 layers. The magnitude of this coupling $J_\perp$ however could not be determined. Just recently Stern *et al*[6] have used Spin Echo DOuble Resonance (SEDOR) to detect interlayer coupling in the normal state of $Y_2Ba_4Cu_7O_{15}$. An estimate of the exchange constant between layers was 55 K. Also more recent neutron scattering measurements of the optic spin wave mode[7] have yielded values of $J_\perp \simeq 0.1 J_{||}$.

In this paper we report on SEDOR measurements taken on the three–layer Pb–doped bismuth compound Bi2223. A useful feature of the three layer compounds is that the local environment about the Cu nuclei in the middle layer is different from that in the sandwiching layers resulting in slightly different NMR frequencies for the two inequivalent sites[8]. Thus a double resonance technique can be used to probe the coupling between Cu moments on the middle and sandwiching layers. We have made measurements at temperatures (10K & 15K) well below the transition temperature T_c = 110 K. This allows us to observe not only the effects of intra and interlayer coupling but also of quasi–particle correlations in the superconducting state.

Coupling of the Cu nuclei occurs via hyperfine coupling and the exchange coupling of localized moments as described by the hamiltonian

$$\mathcal{H} = \mathbf{I_1} \cdot \mathbf{A} \cdot \mathbf{S_1} + \mathbf{I_2} \cdot \mathbf{A} \cdot \mathbf{S_2} + J\mathbf{S_1} \cdot \mathbf{S_2} \tag{1}$$

where A is the hyperfine coupling constant. This can be reduced to the effective hamiltonian

$$\mathcal{H} = \mathbf{I_1} \cdot \mathbf{a} \cdot \mathbf{I_2} \tag{2}$$

in the limit of $J \gg A$. For the field aligned with the principal axes $a_{\alpha\alpha} = A^2_{\alpha\alpha}/2J$. As the coupling constant a relies on quasiparticle exchange between the two Cu nuclei, only the quasiparticle component in the superconducting state will contribute to a. Also the superconducting coherence length ξ_{sc} must be at least of order a lattice constant. As our measurements can distinguish between intra and interlayer coupling we are sensitive to the anisotropy in ξ_{sc}. Further details on the influence of the superconducting state are given below.

Coupling between nuclear spins can be detected by observing the effect a perturbation to one spin species has on another. Clearly if the two spin species are not coupled the perturbation will have no effect. In our SEDOR experiments the Cu(2) spins in the sandwiching CuO_2 layers are monitored with a standard spin echo sequence $\pi/2$—τ—π—τ—echo at frequency $\nu_L(2)$. The Cu(1) spins are perturbed with a π pulse at a time T_{flip} after the first pulse at frequency $\nu_L(1)$. As discussed by Slichter[9] the Cu(2) spin echo will decrease in magnitude as T_{flip} increases due to incomplete refocusing. The amplitude dependence on T_{flip} is given by $cos(aT_{flip})$ for two I=1/2 spins coupled with coupling constant a.

In the case of Bi2223 the linewidths are large enough that not all of the spins can be excited with practical RF pulses. The inset to figure 1 shows the two resonances for Cu(2) and Cu(1) spins with the magnetic field lying in the CuO_2 layers. As a result some of the Cu(2) spins monitored may not have a Cu(1) neighbour which has been affected by the flip pulse. In addition, copper has two natural isotopes. The echo amplitude decays like $1 - P(aT_{flip})^2/4$ for $I = 3/2$ where P describes the conditional probability of a monitored Cu(2) spin encountering a flipped spin on a neighbouring Cu(1) site. Holding the monitoring frequency $\nu_L(2)$ fixed we vary the flip frequency at constant magnetic field. Displayed in figure 1

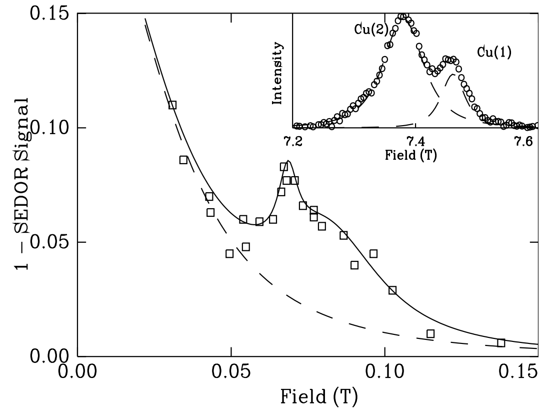

FIG. 1. SEDOR signal as a function of $\nu_L(1)$ at T=10K. Inset is ^{63}Cu NMR central transition spectrum for $\mathbf{H}_0 \perp \mathbf{c}$. Dashed lines are fits indicating the Cu(2) and Cu(1) resonances.

is the SEDOR signal which is the normalized echo for T_{flip} just less than τ. Comparing this with the ^{63}Cu resonances it is evident that both intra and interlayer coupling are present. The solid line is a fit of three modified lorentzians with the dashed line representing the background from Cu(2) interlayer coupling only. The other two components centred near 0.07T are due to interlayer coupling to Cu(1) spins. Each of the three signal components will be discussed below.

Quantitative analysis requires that we link a, which can be extracted from the SEDOR data, to the exchange constant $J_\perp$. The probability P must also be calculated. This quantity is inherent to the nature of the SEDOR spectrum. In order to understand the origin of the three components to the SEDOR signal we first discuss the nature of the inhomogeneous broadening of the Cu resonances.

To determine the actual probability of flipping the neighbouring spin of a monitored spin requires some knowledge of the broadening mechanism involved. Ultimately we need to know the probabilities of affecting a neighbouring Cu(1) spin P_1 and that of a Cu(2) spin P_2. We evaluate parameters at the Cu(1) resonance peak $\nu_L(1)$. Previous work[10] has shown that the inhomogeneous quadrupolar broadening is a direct result of Pb–doping. The Electric Field Gradient (EFG) at a particular Cu(2) and adjacent Cu(1) site is largely determined by the presence of either a Bi^{+3} or Pb^{+2} ion connected to the apical oxygen of the Cu(2) site. Thus we expect the EFG at the adjacent Cu(1) site to be strongly correlated with the EFG at the Cu(2) site. Likewise we expect that the EFG of a neighbouring Cu(2) site to be more or less randomly distributed. Hence the probability of flipping a neighbouring Cu(2) spin is

$$P_2 = \nu_{H_1} Int_2(\nu_L(1)) / \int Int_2(\nu) d\nu \tag{3}$$

where $Int_2(\nu)$ is the intensity of the fitted Cu(2) line as shown in the inset of figure 1. This also holds for a Cu(1) site which is not directly below the Cu(2) site. The spectral bandwidth of the flipping pulse is ν_{H_1}. On the other hand the conditional probability of flipping an adjacent Cu(1) spin is just one as $\Delta\nu(1) < \Delta\nu(2)$ and the spectral width is the same for both nuclei.

The SEDOR spectrum in figure 1 is composed of three distinct components. The narrow peak near 0.07 T has a width (50 KHz) comparable to the pulse spectral width (56 KHz). Hence it can be assigned to interlayer coupling between adjacent Cu(1) and Cu(2) spins. The broader component has a width (300 KHz) similar to the Cu(1) linewidth (340 KHz) indicating it is a result of coupling between Cu(1) spins which are further neighbours to the Cu(2) site. Finally the quickly varying background (dashed line) is due to intralayer coupling between Cu(2) spins. The fitted width of this component (440 KHz) is consistent with the Cu(2) linewidth (570 KHz) shown in the inset to figure 1.

In order to confirm this view on the correlations between spin frequencies we have performed two checks. One was to measure the SEDOR signal on the low field side of the Cu(2) resonance, *i.e.* on the other side from the Cu(1) resonance. This result, with a lower but non zero value, supports our view that the neighbouring Cu(2) flipping probabilities are random and follow the Cu(2) lineshape. The other experiment was to flip at the Cu(1) peak and increase the spectral width of the flipping pulse. This resulted in an increase of the SEDOR signal consistent with an increase in the number of Cu(2) neighbours being flipped without any increase in the number of adjacent Cu(1) nuclei being flipped.

Expecting the interlayer coupling to be considerably weaker than the intralayer coupling one might wonder why the interlayer SEDOR signal is comparable in magnitude to the intralayer SEDOR signal. This is due to an enhancement of the effective interlayer coupling due to the strong AF correlations in the CuO_2 planes. Naively one can view this enhancement as a result of all the adjacent interlayer Cu(1)–Cu(2) spin pairs within a correlation length having in–phase interlayer correlations. Based on this argument the enhancement should be proportional to $(\xi/a)^2$ where ξ is the spin correlation length and a the planar lattice constant. Millis and Monien[11] have developed a model to describe the interlayer coupling $J_\perp$ in reference to the 2D susceptibility χ_i. Here we modify their model to the three layer case where the susceptibility is given by

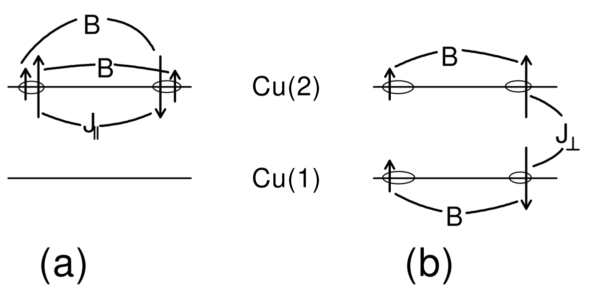

FIG. 2. Hyperfine and exchange coupling for (a) intra and (b) interlayer coupling. Cu nuclear spins are represented with the short arrows and electron moment with the long arrows. Here $\mathbf{H}_0 \perp \mathbf{c}$.

$$\boldsymbol{\chi}^{-1} = \begin{pmatrix} \chi_2^{-1} & J_\perp & 0 \\ J_\perp & \chi_1^{-1} & J_\perp \\ 0 & J_\perp & \chi_2^{-1} \end{pmatrix} \tag{4}$$

where χ_i is the inherent susceptibility of the $Cu(i)O_2$ layer. In the limit of small coupling, $J_\perp \chi_1 \ll 1$, we find the intralayer susceptibility is just χ_1 for the middle layer and χ_2 for the sandwiching layers. The susceptibility perpendicular to the planes is $\chi_{12} = J_\perp \chi_1 \chi_2$.

Calculating the coupling parameters a_{12} and a_{22} in terms of χ_{12} and χ_2 will provide a way to link the SEDOR signal to $J_\perp$. We use the model of Pennington and Slichter[12] to describe the nuclear spin–spin coupling, suitably modified to the three–layer case. The MMP model[13] is used to describe χ_i. Using the hyperfine and other parameters appropriate to this compound we calculate the coupling coefficients appropriate to the broad Cu(1) and Cu(2) lines. In this orientation it has been determined[8] that the onsite hyperfine constant $A_\perp \simeq 0$ so that the transferred hyperfine constant B dominates. Illustrated in figure 2 is the nature of the hyperfine and exchange coupling for intra and interlayer coupling. The only unknown parameter in this model is $J_\perp$. Asymptotically we find that a_{12} is proportional to $(\xi/a)^2$ as expected of interlayer enhancement. In addition to the exchange coupling of nuclear spins we also include the effect of direct nuclear dipolar coupling a^{dip}. As $a^{dip} \propto r^{-3}$ this contribution drops off much faster with distance than a_{ij}. At the nearest neighbour site the dipolar contribution to a_{12} is 85% of the exchange contribution.

The coupling constant $a_{ij}(x,y)$ is calculated for spin $\mathbf{I_2}$ at each lattice site (x,y) taking spin $\mathbf{I_1}$ to be at the origin $(0,0)$. Then a_{ij} is calculated as the appropriate lattice sum. For the narrow SEDOR line due to interlayer coupling to adjacent spins, $a_{12} = a_{12}(0,0)$. The other two broader signals randomly sample the $a_{ij}(x,y)$ distribution whereby $a_{ij}^2 = \sum'_{x,y} a_{ij}(x,y)^2$. It is assumed that the probability P of exciting a particular spin at (x,y) is independent of position (excluding $(0,0)$).

As we are working in the superconducting state the exchange contribution only occurs in the normal regions of the sample. In the context of the two fluid model, with a fraction x_n of normal fluid, there is a factor of x_n which must be considered in addition to the probability P. At low temperatures the dominant contribution to x_n is from impurities. This effect has been studied in some detail, see for example Moler *et al.*[14], where it seems that there is a temperature independent contribution to x_n which is sample dependent. Hardy *et al.*[15] have found that their microwave penetration depth measurements on YBCO crystals required a value for x_n of up to 0.05. As our Bi2223 powders are not of the same quality as Hardy's crystals we expect x_n to be notably larger. As x_n is dominated by impurities at low temperature the quasiparticle distribution can be considered to be static, allowing us to treat a portion x_n of the sample to be in the normal state. This is the other parameter we must determine from our analysis. The Cu(1) and Cu(2) SEDOR signals will allow us to do this.

Including dipolar coupling a^{dip} the SEDOR signal is given by

$$1 - (1-x_n)P/4(a_{ij}^{dip} T_{flip})^2 - x_n P/4(a_{ij}^{dip} + a_{ij})^2 T_{flip}^2 \tag{5}$$

where P contains the isotopic and spectral width contributions. The Cu(2) intralayer SEDOR signal with a_{22} does not depend on $J_\perp$ and hence can be used to determine x_n. We find that $x_n \simeq 0.47$. Using this value of x_n we find for the broad Cu(1) SEDOR signal that $J_\perp \simeq 43$ K. The largest component of uncertainty in this analysis is the determination of the Cu(2) background SEDOR signal. As well there is the typical uncertainty of 20% in the hyperfine coupling constants. Overall the estimate of $J_\perp$ is determined to within a factor of two. Likewise for the estimate of x_n which seems to be somewhat large here. As the two parameters appear as $x_n J_\perp^2$ a reduction of x_n by a factor of 2, for example, would increase $J_\perp$ by 1.4.

Observing any SEDOR signal at all requires a superconducting coherence length ξ_{sc} at least the size of a lattice constant. If ξ_{sc} is short enough it would have the effect of lowering the exchange enhancement between adjacent spins. Thermodynamic values for the intralayer coherence length are in the range $10\mathring{A} < \xi_{||} < 15\mathring{A}$ which is considerably larger than the nearest neighbour separation. On the other hand the interlayer coherence length is typically $\xi_\perp = 3 - 5\mathring{A}$ which is just over the adjacent CuO_2 layer spacing of $3.2\mathring{A}$. Hence the superconducting state should not have the effect of reducing the effective exchange constant. If this were to occur it would reduce the effective spin correlation length thereby decreasing the interlayer enhancement factor. Increasing the temperature does not affect the coherence length much at these low temperatures. As illustrated in figure 3 the normalized SEDOR signals for $T = 10K$ and $T = 15K$ are identical. The independence of the SEDOR signal with

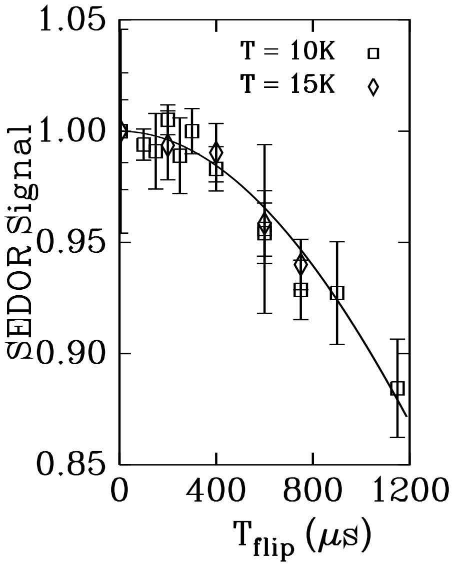

FIG. 3. SEDOR signal as a function of T_{flip}. T = 10K for squares and T = 15K for diamonds.

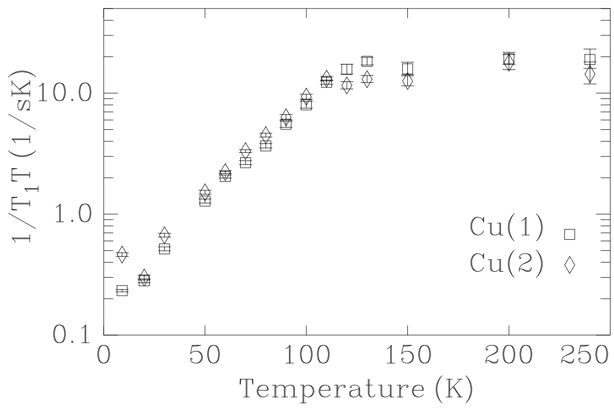

FIG. 4. Spin–lattice relaxation rate for the inner (squares) and sandwiching (triangles) layer Cu spins.

temperature suggests that the coherence lengths and impurity dominated x_n are temperature independent in this range as expected.

In order to relate the exchange constant determined here to its value in the normal state we would like to extend the measurements to higher temperatures. Given the linewidths and ever decreasing T_2 this is not feasible for Bi2223. With sufficiently strong interlayer correlations in the superconducting state we expect the effective a_{12} to be temperature independent. Another indication that strong interlayer correlations exist is the temperature dependence of the spin–lattice relaxation rate $T_1^{-1}(T)$. Figure 4 demonstrates that T_1^{-1} has the same temperature dependence in both the middle and sandwiching layers despite the fact that their physical properties are quite different[8]. The most striking difference is the spin component of the Knight shift which is 2.5 time larger in the sandwiching layers than in the middle layer. This $T_1^{-1}(T)$ data provides reason to believe that strong interlayer correlations exist between adjacent CuO_2 layers in the superconducting state. Hence it is reasonable to expect that the low temperature measurement of $J_\perp$ should reflect the normal state value.

In conclusion we have used SEDOR to compare the Cu nuclear spin coupling both in and between adjacent CuO_2 layers in the superconducting state. A value of the interlayer exchange constant has been extracted: $J_\perp \simeq$ 43 K. Spin–lattice relaxation measurements reveal a close tracking between the middle and sandwiching layers indicative of strong interlayer correlations for all temperatures below T_c.

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