Nuclear magnetic resonance of Tl in superconducting $TlBa_{2-x}La_xCuO_{5-y}$

1992 J. Phys.: Condens. Matter 4 6971

(http://iopscience.iop.org/0953-8984/4/33/010)

J. Phys.: Condens. Matter 4 (1992) 6971–6976. Printed in the UK

Nuclear magnetic resonance of Tl in superconducting $TlBa_{2-x}La_xCuO_{5-y}$

A K Rajarajan†, A Sundaresan‡, Ravi Kumar†, M Sharon‡, L C Gupta† and R Vijayaraghavan†

† Tata Insitute of Fundamental Research, Colaba, Bombay 400 005, India
‡ Indian Institute of Technology, Powai, Bombay, 400 086, India

Received 26 February 1992

Abstract. Results of our nuclear magnetic resonance measurements on two superconducting materials, namely, $TlBa_{1.8}La_{0.2}CuO_{5-y}$ and $TlBa_{1.5}La_{0.5}CuO_{5-y}$ (T_c = 45 K and 32 K respectively) are reported. The most significant finding of the present work is that the nuclear relaxation rate deviates from Korringa behaviour at a temperature much higher than the superconducting transition temperature T_c. An increase in the linewidth is observed below T_c which is due to the formation of the vortex lattice.

1. Introduction

Thallium-based high-T_c superconducting materials may be classified into two categories, namely those containing *one* Tl–O layer and the ones that contain *two* Tl–O layers in the unit cell. Within each category, the superconducting transition temperature T_c depends upon the number of $Cu–O_2$ layers in the unit cell. For each of the members of either of the two series of these compounds, there is an optimum concentration of oxygen that leads to the highest superconducting transition temperature.

Nuclear magnetic resonance (NMR) studies have been extremely useful in obtaining a deeper insight into the nature of the normal state as well as the superconducting state of high-T_c materials. For instance, from the nuclear quadrupole resonance measurements, it follows directly that the copper ions occupying Cu(I) and Cu(II) sites in the crystal structure of the so-called 1–2–3 ($RBa_2Cu_3O_7$; R = Y and rare-earth ions except Ce, Pr, Tb and Lu) superconducting materials do not carry a time-averaged magnetic moment. Asayama *et al* [1] have pointed out a possible correlation between the nuclear quadrupole resonance (NQR) frequency of copper nuclei in many high-T_c superconductors; namely, the higher the T_c, the lower the NQR frequency. Relaxation rates of various nuclei have been measured in a variety of high-T_c materials and important conclusions have been drawn with respect to the nature of Cooper pairing and the magnitude of the energy gap in the superconducting state.

Many NMR studies of Tl nuclei in bilayered Tl compounds have been reported [2–6]. For instance, the nuclear relaxation rate T_1^{-1}, measured in the normal state, of the ^{205,203}Tl isotopes in $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ does not follow the Korringa law

$$T_1T = \text{constant}$$

where T is the temperature of the material. This behaviour, which is similar to what one observes for $^{63,65}Cu$ isotopes in $YBa_2Cu_3O_7$, has important implications with respect to the nature of the normal state (whether Fermi liquid or otherwise) of the high-T_c superconducting materials. Below T_c, the relaxation rate decreases with temperature, indicating a pairing of carriers, but the temperature dependence of the relaxation rate does not follow the trend predicted by the conventional BCS model. In some Tl–O bilayered compounds, the deviation of the relaxation rate from normal behaviour occurs above T_c. We considered it to be of interest to extend our measurements to Tl-based superconducting materials having Tl–O monolayers. In this paper we present results of our Tl NMR studies on La-substituted systems $TlBa_{1.8}La_{0.2}CuO_{5-y}$ and $TlBa_{1.5}La_{0.5}CuO_{5-y}$ which have single Tl–O and also single Cu–O layers.

2. Experiment

Samples of $TlBa_{2-x}La_xCuO_{5-y}$ ($x = 0.2, 0.5$) were prepared by heating together required amounts of the oxides Tl_2O_3 (99.99%), BaO_2 (99.5%), La_2O_3 (99.99%) and CuO (99.99%) in a sealed gold tube [7, 8]. X-ray diffraction showed that the materials were essentially of single phase (see figure 1), except for the presence of traces of $BaCO_3$ (* in figure 1) and $BaCuO_2$ (• in figure 1). Comparison of the strength of the 100% intense peak of the compound with that of the traces of $BaCO_3$ and $BaCuO_2$ suggests that the phase purity of the sample is about 95%. Superconducting behaviour was investigated via the AC susceptibility, measured as a function of temperature; T_c was determined to be 32 K and 45 K for samples with $x = 0.5$ and $x = 0.2$ respectively.

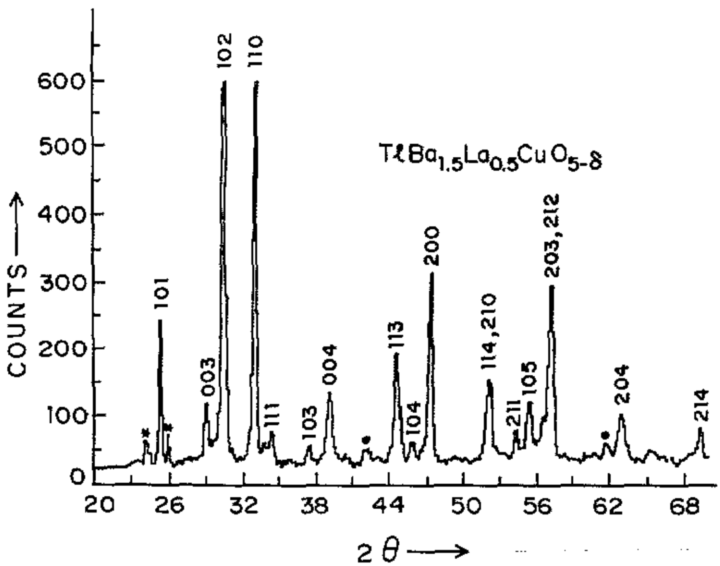

Figure 1. X-ray diffraction pattern of $TlBa_{2-x}La_xCuO_{5-\delta}$. * indicates peaks belonging to traces of $BaCO_3$ and • indicates peaks belonging to traces of $BaCuO_2$.

A standard coherent pulsed NMR spectrometer was employed to study the NMR of ^{203}Tl and ^{205}Tl as a function of temperature ($4.2\ K \leqslant T \leqslant 300\ K$). A liquid helium continuous flow cryostat was used to carry out NMR measurements as a function of temperature. $\pi - \tau - \pi/2 - \tau_0 - \pi - \ldots$ pulse sequence was used to measure the spin–lattice relaxation time T_1. The sample temperature was measured using a Au–Fe0.07%–chromel thermocouple to within an accuracy of 1 K. The magnetic field, held constant at 1.26 T, was calibrated using $Tl_2(SO_4)_3$ as a reference material.

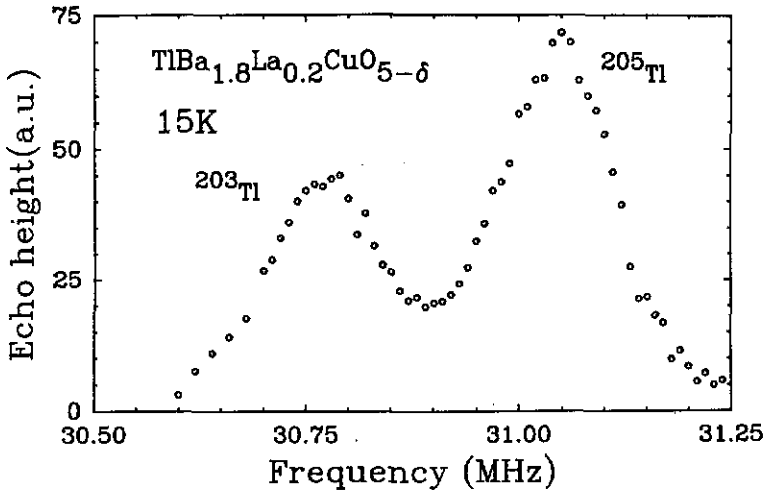

Figure 2. $^{203,205}Tl$ NMR spectrum of $TlBa_{1.8}La_{0.2}CuO_{5-\delta}$ taken at 15 K in a field of 1.26 T.

3. Results and discussions

Figure 2 shows a resonance signal of ^{203}Tl and ^{205}Tl in $TlBa_{1.8}La_{0.2}CuO_{5-y}$ recorded at 15 K. A similar spectrum was also observed in the other material. The Knight shift (K), measured with respect to $Tl_2(SO_4)_3$, is positive (resonance shifted to higher frequency) and essentially independent of temperature in the normal state. This is expected if the normal state of these materials is Fermi-liquid-like. The shift measured at 300 K for the two samples is 0.32%. In the superconducting state K decreases to 0.11% and 0.16% for $x = 0.2$ and 0.5 respectively.

The linewidth ($\Delta\omega$) of the ^{205}Tl resonance is $\sim$ 60 kHz at 300 K. It is weakly temperature dependent in the normal state down to T_c. Below T_c, $\Delta\omega$ starts increasing rapidly and at 4.2 K, it becomes nearly three times its value at 300 K. Figure 3 shows a detailed temperature dependence of $\Delta\omega$. This increase in the linewidth is due to the formation of a flux line lattice in the superconducting state as is usually the case with superconducting materials [9].

Figure 4 shows the relaxation rate T_1^{-1} of ^{205}Tl in the two materials measured as a function of temperature. It is clear that T_1^{-1} follows a Korringa-like behaviour

$$T_1^{-1}(T) = A_0 + A_1 T$$

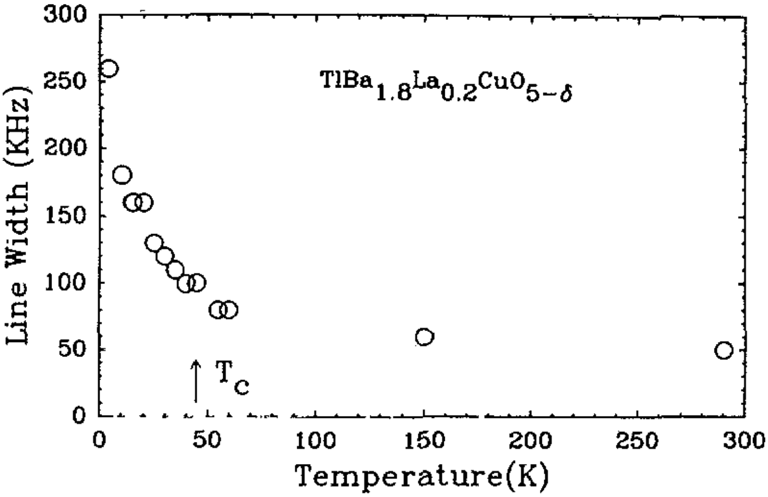

Figure 3. Temperature dependence of the linewidth in $TlBa_{1.8}La_{0.2}CuO_{5-\delta}$. Note that unlike the relaxation rate, see figure 4, the linewidth deviates from normal behaviour at T_c.

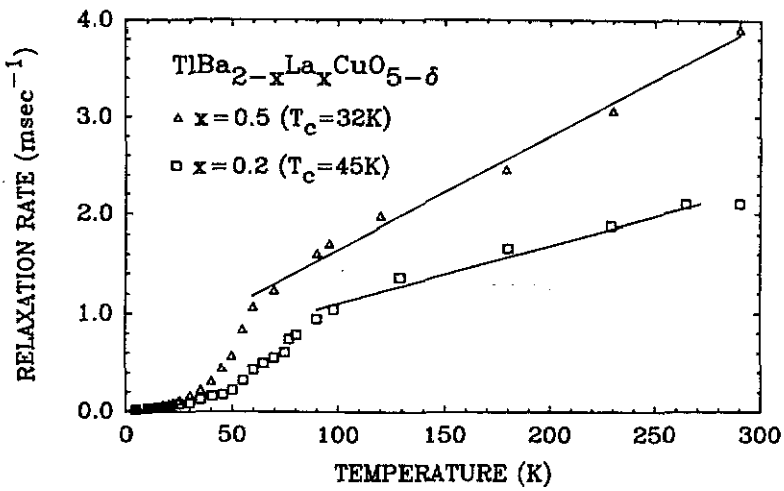

Figure 4. Relaxation rate as a function of temperature for compounds with $x = 0.2$ and 0.5. The normal state shows Korringa-like behaviour. The relaxation rate deviates from normal behaviour at a temperature much higher than T_c. For further details see text.

in the temperature interval 300 K $\leqslant T \leqslant T^*$; T^* ($\simeq$ 60 K and 90 K for the samples with $x = 0.2$ and 0.5 respectively) *being much higher* than T_c. At temperatures below T^*, $T_1^{-1}(T)$ deviates from this linear behaviour. For an ideal Fermi-liquid system, A_0 has to be zero since there are no elementary excitations at zero degrees absolute. Giovanni *et al* [10] obtained the modified Korringa relation for metallic systems in which dilute magnetic impurities are present. According to [9], the Korringa relation gets modified due to the presence of magnetic moments and can be written as

$$1/T_1 = (1/T_1)|_{\mathrm{Korr}}[1 + (6/\pi)(J/E_F)(J/\gamma_e \hbar H)\langle S_z \rangle C].$$

Where J is the s–d exchange coupling constant between magnetic ions and the conduction electrons, C is the concentration of magnetic ions, $\langle S_z \rangle$ the average spin polarization of a magnetic ion in the applied field H. Since $\langle S_z \rangle / H$ is inversely proportional to T the second term leads to a temperature-independent relaxation rate. A possible source of the term A is the presence of dilute isolated magnetic-moment-bearing impurities. We believe that this is rather unlikely in the present studies. Slichter *et al* [11] correlate this additional relaxation rate to fluctuations of Cu d spins in Y123 compounds.

In conventional superconductors, nuclear relaxation occurs via the electron–nuclear contact hyperfine interaction. This leads to two important consequences:

(i) enhancement in the relaxation rate, the so-called Hebel–Slichter peak [12], just as the sample enters in the superconducting state;
(ii) deviation, at and below T_c, of the relaxation rate from the normal-state Korringa behaviour.

Well below T_c, the relaxation rate decreases exponentially with temperature as

$$T_1^{-1} \sim \exp(-E_g/k_B T)$$

where E_g is the energy gap in the superconducting state.

In the present studies, the relaxation rate deviates from the Korringa-like behaviour at a temperature T^* ($> T_c$) and does not exhibit an anomaly at the superconducting transition temperature. Moreover, well below T_c, the relaxation rate does not follow the temperature dependence as suggested by this relation.

In view of the basic differences between the temperature dependences of the measured T_1^{-1} in the two materials and that usually observed in a conventional superconductor, we suggest that there must be another channel of nuclear relaxation besides the electron–nuclear contact hyperfine interaction. The contribution arising due to this channel must be quite significant in order to account for the differences, both in the normal state and the superconducting state, mentioned above. It has been suggested [11, 13] that there are antiferromagnetic fluctuations in high-T_c materials that give rise to an important contribution to the nuclear relaxation rate. The results of our measurements are consistent with the existence of antiferromagnetic fluctuations in the two materials.

It is instructive to note that the resonance linewidth increases rapidly as the sample is cooled below T_c and not T^*. This is consistent with the fact that the variation in the linewidth occurs only when the sample enters into the superconducting state. In conventional superconducting materials, deviation of the relaxation rate from the Korringa behaviour as well as the increase of linewidth occur at and below T_c.

4. Conclusions

The Knight shift, linewidth and relaxation rate of ^{205}Tl NMR have been measured in two single-Tl–O layer systems $TlBa_{1.8}La_{0.2}CuO_{5-y}$ and $TlBa_{1.5}La_{0.5}CuO_{5-y}$ (T_c = 45 K and 32 K respectively) in the temperature interval 300 K $> T >$ 4.2 K. The Knight shift is independent of temperature in the normal state but decreases in the superconducting state. The relaxation rate shows significant departure, both in the normal as well as in the superconducting state, from the behaviour observed in conventional superconductors. Antiferromagnetic fluctuations may be responsible for this behaviour. The resonance linewidth increases rapidly below T_c just as in a conventional superconductor.

References

[1] Asayama K, Zheng G-Q, Kitaoka Y, Ishida K and Fujiwara K 1991 *Physica* C **178** 281–6
[2] Hentch F, Winzek N, Mehring M, Mattausch Hj, Simon A and Kremer R 1990 *Physica* C **165** 485
[3] Mehring M, Hentsch F and Winzek N 1990 *Springer Series in Solid State Sciences* vol 99, ed H Kuzumany, M Mehring and J Fink (Berlin: Springer) p 184
[4] Fujiwara K, Kitaoka Y, Asayama K, Shimakawa Y, Manako T and Kubo Y 1990 *J. Phys. Soc. Japan* **59** 3459
[5] Kitaoka Y, Fujiwara K, Ishida K, Asayama K, Shimakawa Y, Manako T and Kubo Y 1991 *Physica* C **179** 107–18
[6] Hentsch F, Winzek N, Mehring M, Mattausch J and Simon A 1989 *Physica* C **158** 137
[7] Subramanian M A, Calabrese J C, Torardi C C, Chowdry U and Sleight A W 1988 *Nature* **332** 420
[8] Sundaresan A, Rajarajan A K, Gupta L C, Sharon M and Vijayaraghavan R 1991 *Physica* C **178** 193–6
[9] Pincus P, Gossard A C, Jaccarino V and Wernick J H 1964 *Phys. Lett.* **13** 21
[10] Giovanni B and Heeger A J 1969 *Solid State Commun.* **7** 287
[11] Slichter C H and Pennington C P 1990 *Physical Properties of High Temperature Superconductors* ed D M Ginsburg (Singapore: World Scientific) p 269
[12] Hebel L C and Slichter C P 1959 *Phys. Rev.* **113** 1504
[13] Millis A J, Monien H and Pines D 1990 *Phys. Rev.* **42** 167