Charge Distribution in (Tl,Pb)Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{9-δ} (T\textsubscript{c}=124K): an $^{17}$O NMR Study

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$^{17}$O NMR measurements on (Tl,Pb)Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{9-δ} (T\textsubscript{c}=124K) show that the Knight shift of the outer two Cu-O planes (with pyramidal coordination for copper) has a very different behavior to that of the inner plane (with square coordination for copper). The former has a larger magnitude and a weaker temperature dependence in the normal state, whereas the latter is smaller but has a stronger temperature dependence, implying a nonhomogeneous charge distribution and a weak interaction among the Cu–O layers. The results are compared with those for (Bi,Pb)\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10-δ} (T\textsubscript{c}=107K) and Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10-δ} (T\textsubscript{c}=125K).

NMR is a powerful probe for the study of the local and low energy spin excitations in high-T\textsubscript{c} copper oxides. Since it is universally accepted that the electronic properties are dominated by the Cu–O planes, NMR studies of copper and oxygen attract the most attention. The fact that $^{17}$O (I=5/2) has a quadrupole moment an order of magnitude smaller than that of $^{63}$Cu (I=3/2) makes it more useful in studying samples for which large size single crystals are not available and magnetic alignment of powders is difficult to achieve. NMR measurements of the $\frac{1}{2} \rightarrow \frac{3}{2}$ central transition on polycrystalline samples of the triple layered (Bi,Pb)\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10-δ} (Bi2223, T\textsubscript{c}=107K) [1,2] have shown that the $^{17}$O shift for the outer two Cu-O planes has a larger magnitude and a weak T dependence in the normal state, whilst the shift for the inner plane is smaller but has a stronger T dependence. This implies different spin susceptibilities or hole densities for the outer and inner Cu–O planes with the inner plane having a lower susceptibility. Recent $^{17}$O [3] and $^{63}$Cu [4] NMR studies of Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10-δ} (Tl2223, T\textsubscript{c}=125K), which is structurally similar to Bi2223, have revealed only a single spin susceptibility exists for both the outer and inner Cu–O planes, suggesting a uniform charge distribution and strong coupling among the Cu–O planes in this system. The crystal structure of (Tl,Pb)Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{9-δ} (Tl2223, T\textsubscript{c}=124K) is similar to that of Tl2223 (Bi2223). The main difference is that the double Tl–O (Bi–O) layers in Tl2223 (Bi2223) are replaced by a Tl/Pb–O monolayer in Tl1123. In this paper we report $^{17}$O NMR results obtained for Tl1123 in an attempt to understand the relation between the charge distribution and superconductivity in multiple Cu–O layered systems.

The Tl1123 sample used in this work had a T\textsubscript{c} of 124K (before the oxygen enrichment) and is almost of single phase according to X-ray diffraction, Energy Dispersive Spectrometry and magnetization measurements. Details about the sample preparation and characterization have been published elsewhere [5]. NMR measurements were performed with a Bruker MSL 360 spectrometer operating at 8.45 T. Shifts were determined externally relative to tap water.

NMR studies on powder materials by different groups have revealed some common features in the $^{17}$O spectra for different high-T\textsubscript{c} copper oxides such as Bi\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{1−δ}Cu\textsubscript{2}O\textsubscript{4+2n} (n=1,2,3). There are generally two distinct shift ranges for oxygens in two different environments: (diamagnetic) resonances at 200–500 ppm for oxygens in insulating layers whereas (paramagnetic) resonances at 1200–2000 ppm for oxygens in the conducting Cu–O planes.

Figure 1 shows the room temperature $^{17}$O spectrum for Tl1123 (b), together with those for Bi2223 (a, [1]) and Tl2223 (c, [3]). A broad resonance near 250 ppm for Tl1123 is similar to that for Tl2223 and is attributed to the (Tl,Pb)/Sr–O layer oxygens. Interestingly, Tl1123 has two resonance lines in the paramagnetic region resembling Bi2223 rather than Tl2223. The resonance at 1900 ppm is...
thus assigned to the oxygens in the outer two Cu–O planes (with pyramidal coordination for copper) and that at 1300 ppm to the inner plane (with square coordination for copper). The 1900 ppm line for Tl1223 is narrower than in Bi2223 indicating a smaller shift anisotropy. This may be due to the fact that the outer planes in Tl1223 are flatter.

Figure 2 shows the $^{17}$O shifts for the outer (triangles) and inner (squares) Cu–O planes in Tl1223 as a function of temperature. (The shift for the insulating (Tl,Pb)/Sr–O layer does not change with temperature apart from demagnetisation effects below $T_c$.) The shift for the outer planes does not vary much with temperature until just above $T_c$, where it starts to decrease rapidly. Whereas the $T$ dependence of the shift for the inner plane is strong, it decreases with lowering temperature and it has dropped to about 2/3 of its room temperature value by $T_c$. The overall behavior of the shifts for Tl1223 is very similar to that for Bi2223.

The similarity of the magnetic behavior of Tl1223 to that of Bi2223 thus indicates that the charge distribution in Tl1223 is not homogeneous, contrary to the case of Tl2223 where a uniform charge distribution exists among the outer and inner Cu–O planes. In these systems, which all have a very similar structure, Tl2223 has the highest $T_c$ (125 K) compared with 107 K for Bi2223 and 124 K for Tl1223. This suggests that the combination of homogeneous charge distribution and strong interactions among the Cu–O planes may be essential for achieving a higher $T_c$ in a multiple layered system [3,4].

This work has been supported by the SERC.

REFERENCES

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