Further measurements on the Tl0.5Pb0.5Sr2(Ca1−yYy)Cu2O7−δ system
Pb NMR and magnetic susceptibility

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Abstract

Susceptibility data are presented for the septenary alloy system Tl0.5Pb0.5Sr2(Ca1−yYy)Cu2O7−δ (0 ≤ y ≤ 0.5), together with Pb NMR. The earlier hypothesis that over the metallic alloy range at room temperature the spin susceptibility might be constant is shown to be incorrect. In correlating these new data with earlier copper and yttrium NMR data a consistent picture emerges of a one-component system, but with a small (~10%) anisotropy of the spin susceptibility of the copper planes. We show also that there is 89Y p character admixed into the copper hole wavefunctions. The susceptibility shows a pre-cursor drop in all samples at temperatures close to 120 K, well above Tc, perhaps an indication of spin pairing well into the non-superconducting region. This may be spin-fluctuation diamagnetism.

1. Introduction

In a series of articles [1–3] we have explored the properties of the high-temperature superconductor Tl0.5Pb0.5Sr2(Ca1−yYy)Cu2O7−δ as a function of y, 0 ≤ y ≤ 1.0. In the superconductor–metal range, 0 ≤ y ≤ 0.5, the system passes from overdoped to underdoped as the yttrium concentration increases. One feature that has been observed in earlier studies is that, as y varies, the axial Knight shift at the copper site is constant, whereas the isotropic component of the Knight shift has a strong compositional dependence. At that time, we speculated that the cause of these shift dependences on y might be that the spin susceptibility at the copper sites remained constant as the yttrium composition varied, whilst the B term describing the hyperfine coupling between one copper electron spin and its nearest-neighbour nucleus varied with composition.

This paper returns to this topic, presenting new magnetic susceptibility (taken on the SQUID based system at the Royal Institution) and Pb NMR data on the same samples as for previous studies, together with some supplementary copper shift and relaxation data.

2. Results and discussion

The susceptibility data are shown in Fig. 1 for samples y = 0.0, 0.1, 0.2, 0.3, and 0.5. The y = 0.4 sample...
Fig. 1. The measured (SQUID) susceptibility between 100 and 300 K. The vertical, downward pointing arrows represent the feature $T_m$ (Table 1).

Table 1

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$T_m$ (K)</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>115</td>
<td>80</td>
</tr>
<tr>
<td>0.1</td>
<td>120</td>
<td>102</td>
</tr>
<tr>
<td>0.2</td>
<td>145</td>
<td>108</td>
</tr>
<tr>
<td>0.3</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>105</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig. 2. The Pb spin-echo area, taken at room temperature with a point-by-point technique of data acquisition. The inset shows the Pb shift of the peak position relative to a reference position of 104.46 MHz (see text), as a function of $\gamma$.

in this series produced anomalous features in several experiments, and has therefore been left out of this presentation:

1. significant ($\leq 20\%$) intensity appears at peak positions from an unidentified phase in the X-ray power diffraction.

2. The copper NMR of this material produced two peaks of comparable intensity at the 90$^\circ$ orientation of the sample alignment axis with respect to the magnetic field. All the other samples produced predominantly single peaks [4].

3. In the lead NMR, the intensity of the resonance from this material was very low, well outside the trends shown by the other samples.

4. The susceptibility of this 0.4 sample, whilst largely temperature independent, is about twice the size of that for any of the other samples, and again lies far outside the systematic trends with concentration shown by the other samples.

We believe that the $\gamma = 0.4$ sample has been contaminated by a different phase having a high Pauli susceptibility in which the lead nucleus only relaxes slowly (and hence is undetectable) and where the copper Knight shift and/or quadrupole interaction is very different from that in the host phase. Accordingly we leave the data for this sample out of our discussion.

All the data are largely temperature independent above 140 K, with the $\gamma = 0$ sample having the largest susceptibility; from $\gamma = 0$ to 0.2 inclusive the susceptibility shows a monotonic decrease, whilst for $\gamma = 0.3$ and 0.5 the values are similar and comparable to the value for 0.2. This behaviour is peculiar and quite different from the other cuprates such as YBCO.

An interesting feature is the turn-over in each of the curves, marked by the arrows, at temperatures well above the critical temperatures for superconductivity. Table 1 lists these temperatures as $T_m$, together with the $T_c$ values, for each of the samples.

Fig. 2 shows the Pb NMR data at room temperature. There is a small axial component of the shift (see inset). It is however so small that we have not been able to measure it satisfactorily. The main data in Fig. 2 have therefore been taken on samples of randomly oriented powders. We believe that the Pb shifts should be measured from the position for Pb$^{4+}$; the Pb/Tl substitution behaves as though Pb goes in to this septenary system as Pb$^{4+}$. Unfortunately Pb$^{4+}$ only appears in the literature of shifts for PbO$_2$ and PbCl$_4$, with the former material being quoted as metallic. PbCl$_4$ is quoted [6] as having a Pb chemical drift of $+2400$ relative to Pb(NO$_3$)$_2$. If we take the PbCl$_4$ as the origin of our chemical shifts, this resonates in our spectrometer at a frequency of 104.570 MHz. This, however, is approximately the resonance position of the $\gamma = 0.2$ sample, and places half of our metallic samples with positive shifts and a half with negative shifts.
A solution of Pb(NO₃)₂ resonates at 104.321 MHz. This resonance position should be characteristic of Pb²⁺, with a spherically symmetric charge distribution [7].

A third alternative as the Knight shift origin is to use the observation that the resonance positions of the insulating samples y = 0.6, 0.7, 0.8 are independent of y (Fig. 2). This places the origin of the shift at 104.46, just about half way between the other two possibilities. We take this last value as the origin; either the particular environment (coordination shell) or the possibility that PbCl₄ is not completely ionic must account for the difference between our chosen origin and the resonance position of PbCl₄.

With this choice of origin of the shifts, the metallic samples in the series y = 0 to 0.5 exhibit monotonically decreasing Pb Knight shifts, positive in sign. Pb interacts with the CuO₂ planes via the apical oxygens in this structure. The Pb atoms occupy positions relative to the CuO₂ planes very similar to the positions of the Cu (1) atoms in the better known YBa₂Cu₃O₇ structure. The severe loss of Pb integrated intensity in the 0.6, 0.7 and 0.8 samples (Fig. 2) we ascribe to the onset of antiferromagnetism in the CuO₂ plane, which broadens, through small variations of the local environment, without shifting the Pb resonance.

Given the correlation over the whole metallic range between the observed Pb shifts (Fig. 2), and those isotropic shifts already reported for ⁶³Cu [3] the question naturally arises as to whether the one-component model (a correlation between ⁸⁹Y and ⁶³Cu shifts has already been noted [4]) can be extended to ²⁰⁷Pb shifts. We are dealing here with a transferred hyperfine interaction from the Cu spins via the apical oxygen, to the ²⁰⁷Pb nuclei.

Fig. 3 shows the temperature variations of the Pb shift in the temperature range 145 to 300 K for the y = 0 randomly oriented powder sample. The small increase in K shift as the temperature decreases matches the similar trend in the susceptibility, Fig. 1, for this sample. Plotting K against χ with temperature as the implicit variable produces a hyperfine field of (18 ± 5) kG.

The question also arises as to whether, at room temperature, the susceptibility trends in Fig. 1 as a function of composition y correlate with the variation of K; for the y = 0.0, 0.1 and 0.2 samples, indeed K and χ are linked by the same hyperfine field as derived above from the T dependence for y = 0.0 (in this case the hyperfine field works out at (13 ± 3) kG) (However, see later discussion, if this decrease of χₚᵢ𝑛 with composition is partly due to a new phase emerging, then this calculation may be an overestimate). With this corroboration of the hyperfine-field calculations, and the indication that the temperature dependence of χ for y = 0.0 is indeed due to the temperature dependence of the copper–oxygen spin susceptibility, we can now answer the question as to the proportions of the measured susceptibility that are spin/orbital in origin. When the K: χ plot, at room temperature for y = 0, 0.1, 0.2, is extrapolated to χ = 0 an intercept on the K-axis of 0.03 ± 0.03% emerges, whilst if the K: χ plot for y = 0 is extrapolated to x = 0 a very small negative intercept, −0.02 ± 0.05%, emerges. It looks as though the measured susceptibility for y = 0 to 0.2 is a spin susceptibility, and therefore, that the diamagnetic and orbital susceptibilities in this material in this concentration range are roughly equal in magnitude, and opposite in sign.

Since the shifts diminish monotonically as y moves from 0 to 0.5 (Fig. 2), why to the susceptibilities for y = 0.3 and 0.5 not follow the same trend? One possibility is that at the higher values of y in the metallic range a component of susceptibility grows, but does not couple strongly to the Pb or Cu nuclei. As an aside, the general pattern of behaviour of the susceptibility in this material is unusual [8]. As in other high-Tc materials [8], in the overdoped region, y small, the susceptibility is varying strongly with concentration, χ reduces as Tc increases. However, in the underdoped
area, \(y = 0.3\) to 0.5, the susceptibility is rather concentration independent. Furthermore, it is just in the under-doped regime that the correlation between susceptibility and Knight shift breaks down. Finally in the under-, the optimally and the over-doped regimes the susceptibility is at most weakly temperature-dependent. Contrast this behaviour with the common behaviour for most other high-\(T_c\) materials [8], where over-doping is associated with temperature-independence, and under-doping with a strong temperature dependence, of \(\chi\). In this thallium septenary system the temperature dependence of the susceptibility is weak everywhere, but has a definite minimum at \(y = 0.2\) and 0.3 (at both of these concentrations the 150 K and 300 K susceptibilities are identical within experimental error). In the context of comparing this behaviour with that of oxygen-depleted YBCO it is, of course, important to know and compare the amounts of over- and under-doping that are present at the various \(y\) values for the septenary, and at the various oxygen \(\delta\) vacancies in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\). Comparison of Hall numbers of room temperature is not helpful [4]. A simple electron counting process would indicate that at \(y = 0.5\), 0.3 holes have been annihilated/unit cell beyond optimal doping (\(y = 0.2\)). In YBCO, if we take optimal doping as \(\delta = 0.05\), then one is in the equivalent position (to \(y = 0.5\) in the septenary) for a \(\delta\) of 0.2. The susceptibility of YBa\(_2\)Cu\(_3\)O\(_{6.8}\) (\(T_c = 80\) K) has a substantial temperature dependence, as given evidence for by the yttrium Knight shift [8]. Another approach would be to say that in comparing the septenary system and YBCO one should assume that equivalent hole doping is achieved in systems with equivalent \(T_c\) [8]. The \(T_c\) in our septenary system at \(y = 0.5\) is about 45 K; the equivalent YBa\(_2\)Cu\(_3\)O\(_{6.53}\) has a considerable temperature dependence [9]. For example a decrease of temperature from 300 K to 150 K in YBa\(_2\)Cu\(_3\)O\(_{6.53}\) produces a diminution of the susceptibility by \(~30\%\); a similar decrease of temperature in Tl\(_{0.3}\)Pb\(_{0.7}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\)Cu\(_3\)O\(_7\) produces an increase of the susceptibility by about 15%. Thus, no matter how the comparison is made, the susceptibility in the under-doped region of our septenary system does appear to be exhibiting a smaller and different temperature dependence than analogous samples in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\).

There appear to be two problems with our susceptibility results in the under-doped region, \(y = 0.3\) and 0.5: (1) the weak temperature dependence, (2) the breakdown of the correlation, observed for small \(y\), between the susceptibility and the lead and copper (isotropic) Knight shifts.

We speculate that the lead and copper Knight shifts represent the true behaviour of the spin susceptibility in our samples, \(y = 0.3\) and 0.5, which thus continues to decrease as \(y\) increases. This decrease in the spin susceptibility is perhaps, however, masked, in the total susceptibility measurements (Fig. 1), by a roughly equal and opposite rise in a susceptibility contribution from paramagnetic spins, and impurity Curie component, in the \(y = 0.3\) and 0.5 samples. Such a component would have no effect on the Knight shifts, but would tend to broaden the NMR lines, particularly at low temperature. Unfortunately the lowest temperature of our susceptibility measurements is 100 K; lower temperatures would have shown up any Curie tail.

In an earlier paper [2] we discussed the related problems of the drop in integrated copper NMR intensity from \(y = 0.3\) to 0.5, and the disappearance of the thallium signal at low temperature at \(y = 0.4\) and 0.5. Our data (Fig. 2) on lead NMR also show a drop in integrated intensity for \(y = 0.3\) to 0.5. We alluded [2] to the possibility that the yttrium/calcium substitution adds particular magnetic configurations (e.g. the presence of two yttriums in the nearest-neighbour group of four Y/Ca sites to a particular copper), wiping our superconductivity (and hence reducing the superconductivity fraction) and the near thallium and copper resonances. The appearance of an antiferromagnetic phase with low carrier concentration is another possible explanation here.

Thus the lead data (Fig. 2) may add support to our earlier [2] supposition; increasingly, as \(y\) increases above 0.2, volumes of the sample are “taken-out” by the appearance of local moments. We estimate that the 0.5 sample would need to have about 10% of the Ca sites occupied by local moments, in order that the local fields generated would broaden the thallium low-temperature line beyond observability, and yet produce relatively little effect on the width of the Pb resonance at 140 K (Fig. 2). Any Curie tail would be masked in our susceptibility measurements, taken at rather high temperatures, by the appearance of a temperature-dependent spin susceptibility \(X_{\text{spin}}\) characteristic of the observed volume of sample, with \(X_{\text{spin}}\) decreasing as \(T\) decreases in a similar way to observed trends in other
high-$T_c$ superconductors in the underdoped regime [8]. 10% Ca sites with paramagnetic moments would give a Curie contribution at and above 100 K of about the right magnitude. Unfortunately an attempt to measure the lead shift in the $y=0.5$ sample as a function of temperature failed: the NMR lines are too broad and weak to give data of sufficient accuracy. This is a further feature of our data that corroborates the model of magnetic defects at $y \geq 0.3$; the Pb signal intensity grows sharply at $y=0.0$ as temperature down to 140 K, and all the diminishing temperature does is broaden the lines. A steady growth, from $y=0.3$ and above, of an antiferromagnetic fraction is an alternative possibility, especially if this anti-ferromagnetic fraction also varies with temperature.

The sign of the lead shift (Fig. 2) is positive. For a transferred hyperfine interaction a negative sign, via the core-polarisation mechanism, is more normal. The indication is therefore that there is a weak admixture of lead $6s$ character via the apical oxygen, in the copper spin susceptibility. A hyperfine field of the order of 15 kG indicates just how weak this admixture is (of. shift in Pb metal of 1.5%, in by no means an s-character metal).

The small anisotropy of the lead shift commented upon earlier must, for an isotropic hyperfine field, reflect the anisotropy of the electron spin susceptibility. Many treatments of high-$T_c$ superconductors, starting with the classic work of Mila and Rice [10], have assumed that the one-component spin susceptibility is roughly isotropic. We believe, however, that there is significant NMR evidence to cast doubt on this deduction. The anisotropy of the lead shift above is one such piece of evidence; a similar anisotropy has been noted in the $^{89}$Y shifts (Figs. 5 and 6 in Ref. [3]) in this septenary system, and in YBCO [12]. Indeed in the septenary system [3] the anisotropy is rather large at low $y$. For example, at $y=0.2$ and room temperature, the difference between the $^{89}$Y position for $c$ parallel and $c$ perpendicular to the applied magnetic field $B$ is 180 ppm, a large fraction of a total shift $\sim 300$ to 400 ppm. The implication of these yttrium data is that the spin susceptibility at room temperature is about twice as big for $c$ parallel to $B$ as for $C$ perpendicular to $B$. However, the anisotropy effect noted above in the lead NMR is quite small, of the order of 10% of the shift.

Thus we are led to suggest that the $^{89}$Y anisotropy is not only generated by the anisotropy of the spin susceptibility (although this probably contributes) but that a significant proportion may stem from an admixture of $Y^{3+}$ $p$ atomic orbital into the electron states at the Fermi surface, leading to an anisotropic hyperfine field at the yttrium nuclei. Takigawa et al. have already noted an effect of this type [12]. The uncertainty in the zero of the $^{89}$Y shifts prevents us from making this a firm conclusion.

In the light of the above discussion we can now return to an analysis of the shifts at the copper nucleus [3]. Our susceptibility measurements have clearly eliminated the possibility that the spin susceptibility remains constant over the range $y=0$ to 0.5, and the discussion above has reintroduced the probability that the spin susceptibility is anisotropic.

Writing the Knight shift components [10] as

$$K_x = \left[ \gamma_e y_e \hbar^2 \right]^{-1} \times (A_{\text{orb}} \chi_{\text{orb}} + (A_s + 4B) \chi_s + (A_{s,0} + A_{s,0}) \chi_{s,0}) ,$$

where $\alpha=x$, $y$ or $x$, $\chi_s$ is a spin and $\chi_{\text{orb}}$ an orbital susceptibility, we have concluded earlier that the monotonic decrease of $K_{ax}$ with $y$ for $y=0$ to 0.5, indicates that the $\chi_{s,0}$ term is decreasing monotonically in a similar fashion (Fig. 1), with the proviso that for $y=0.3$ and 0.5 this decrease of the spin susceptibility is masked by an increase of a paramagnetic contribution to the susceptibility. What, however, does the constancy of the axial component of the Knight shift, $K_{ax}$, over the same composition range mean? We assume that the orbital component, the first term in the equation above, is constant, so that although a significant fraction of $K_{ax}$ may be due to orbital effects, these effects do not change across the composition range. Then $K_{ax} = K_{ax}^{orb}$, proportional to $K_{ax}$, is given by

$$(A_s + 4B) \left( \chi'_c - \chi_{s,0}^{a,b} \right) + A_{s,0} \chi_{s,0} - A_{s}^{a,b} \chi_{s}^{a,b} + A_{s,0,0} \chi_{s,0}^{a,b}$$

and we know (above) that $(\chi_{s,0}^{a,b} + 2\chi_{s}^{a,b})$ is decreasing with $y$. Given the constraints it is quite possible to envisage scenarios where $K_{ax}$ stays constant; for example if $\chi_{s}^{a,b}$ is constant then $\chi_{s,0}$ must be decreasing, so that $(A_{s,0} + 4B) \left( \chi'_c - \chi_{s,0}^{a,b} \right)$ is decreasing, and positive if $\chi'_c > \chi_{s,0}^{a,b}$. The terms $A_{s,0}^{a,b} \chi_{s,0}$ and $A_{s,0,0}^{a,b} \chi_{s,0}$ will be decreasing in magnitude as $y$ increases, but $A_{s,0}^{a,b}$ is negative [10], so that this term is actually increasing and may
well counterbalance the decrease of the other terms.

We undertook another related $^{63}$Cu NMR experiment on a randomly oriented powder, $y=0$, taking spectra at 296 K and 150 K. The spectra are similar powder (twin-peaked) spectra, with the high-field peak at 134.2 MHz in both, and the low-field peak at 132.95 MHz at room temperature and at 133.18 MHz at 150 K. From our discussion so far we might guess that $K_{ax}$ should stay constant with temperature, and, from the susceptibility measurements (Fig. 1) we would expect that $K_{iso}$ would increase in this temperature range by 12%. We can fit the observed spectrum at 150 K [13] with an increase of $K_{iso}$ of 11% and a decrease of the quadrupole resonance frequency from 20.9 to 19.3 MHz, and, using the assumption that the value of $K_{ax}$ remains constant. However, this decrease in quadrupole resonance frequency is too large, if known temperature coefficients of $\nu_0$ in YBCO and related materials are considered. It looks as though the constancy of $K_{ax}$ occurs only as a function of composition at room temperature.

We turn now to Table 1, where values of the turnover temperature, $T_m$, in the susceptibility data (Fig. 1) are displayed. It is as though the spin pairing starts well above $T_c$ in all cases, only accelerating to completion at $T_c$ itself. Such an effect has been documented before, in experiments on aligned powders of YBa$_2$Cu$_3$O$_7$ [14], and dubbed spin-fluctuation diamagnetism. Unfortunately we are not at present able to do microscopic susceptibility measurements via NMR in this temperature range at the moment.

3. Conclusion

New susceptibility data via a SQUID system in the septenary alloy series Tl$_{0.2}$Pb$_{0.8}$Sr$_2$Ca$_{1-y}$Y$_y$Cu$_2$O$_{8.6}$, $0 \leq y \leq 0.5$, are presented, a series which exhibits superconductivity ranging up to a $T_c$ of 108 K at $y=0.2$. The susceptibility shows a marked dependence on $y$ for $0 \leq y \leq 0.2$, although all susceptibilities exhibit at most a weak temperature dependence.

When these data are correlated with $^{63}$Cu, $^{207}$Pb and $^{89}$Y Knight shift and linewidth data, it appears possible that the roughly concentration and temperature independence of the total susceptibility in the underdoped regime is an artefact introduced by a cancellation of two contributions; a Curie tail and the normal drop (with decreasing temperature and with increasing $y$) in spin susceptibility in the under-doped regime. However, the same data could also be explained by the appearance for $y \geq 0.3$ of antiferromagnetism in a steadily growing fraction of the samples.

The lead nuclei sample the same susceptibility as the copper and yttrium nuclei, and $K^{Pb}:\chi$ plots with both temperature and concentration ($0 \leq y \leq 0.2$) as the implicit variable agree with each other to produce a hyperfine field of about 15 kG. $K^{Cu}$ at $y=0$ also follows the susceptibility as a function of temperature. The positive sign of the Knight shift at the lead nucleus indicates Pb 6s character admixture in the wavefunction at the copper site, a transferred hyperfine interaction via the apical oxygen.

The small observed anisotropy of the lead shift indicates a small, but not zero, anisotropy in the spin susceptibility associated with the copper planes. In this septenary system the strong anisotropy in the $^{89}$Y shifts at low $y$ probably indicates Y p character admixed with the hole on the copper site. We believe such character also exists in YBCO based systems. The susceptibility is observed to drop well before $T_c$ in all metallic samples, $0 \leq y \leq 0.5$. Spin pairing at a temperature $T_m > T_c$ appears to be taking place.

Acknowledgements

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References
