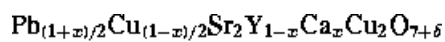


Yttrium and lead nuclear magnetic resonance investigation of a 1212 superconductor,



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Yttrium and lead nuclear magnetic resonance investigation of a 1212 superconductor, $\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2}\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{7+\delta}$

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Received 11 July 1997, in final form 31 October 1997

Abstract. We present NMR experiments on the normal state of the 1212 superconductor $\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2}\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{7+\delta}$; the samples have x -values ranging from 0.2 to 0.5, and most samples have δ -values of zero but there is one sample with a δ -value of 0.1. The bulk magnetic susceptibility for all of the samples presents a temperature variation which can be fitted by the sum of a Curie–Weiss and a Pauli, temperature-independent, term. The ^{89}Y shift and relaxation data are compared to those from the thallium 1212 superconductor, and to those from YBCO, showing a correlation between the shifts and the distances between the yttrium nuclei and the copper oxide planes. We find an unusual dimerization of the yttrium nuclei, strongly temperature dependent, revealed by Meiboom–Gill spin-echo measurements. The ^{207}Pb resonance at room temperature exhibits a significant shift as the x -value (the calcium concentration) is varied, possibly indicating a monotonic variation of the Pb valence.

1. Introduction

There have been many careful studies of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ and related materials in the normal state. Generally, it is possible to separate the observed unusual effects into two groups, just above T_c , and in the higher-temperature range, 180 to 270 K. For the electronic properties, considerable attention has focused on the spin-gap behaviour and its temperature onset, and these effects we classify within the first group, just above T_c (see, for example, reference [1]). Experimental powder x-ray and dc magnetic susceptibility results [2, 3] have been reported recently for a range of high- T_c materials, such as 2201-, 2212-, and 2223-BISCCO, and 123-, 124-YBCO compounds, showing that, if they are approximately optimally doped, then both magnetic and structural anomalies occur at the temperature T' , where T' , different for each compound, lies in the range 180 to 270 K. An important recent contribution to the debate about T' -effects has come from Suter *et al* [4], regarding $\text{YBa}_2\text{Cu}_4\text{O}_8$, for which they suggest that the changes that occur in NMR parameters may be driven by a charge-density-wave instability.

This article presents an analysis, primarily via nuclear magnetic resonance (NMR), of the microscopic properties of a system on which earlier detailed structural studies have taken place [5]. We seek to clarify the relationship between the structural and any magnetic anomalies.

$\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2}\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{7+\delta}$ forms a high-temperature superconducting series as x is varied, with a T_c varying by up to 40 K. Structural stability exists over the range of x between 0 and approximately 0.5, and it has a 1212 structure related to that of YBCO. The annealing conditions play an important role in determining whether the samples superconduct; an increase of oxygen content from 7.0 to 7.1 destroys the superconductivity [6]. All of the superconducting samples are formed by quenching from 800 °C, and we have verified that this procedure gives an oxygen concentration of 7.00 ± 0.01 per formula unit. An interesting aspect of the stable structure is that, as x is varied, and assuming the standard valences Pb^{4+} , Cu^{2+} , Y^{3+} , and Ca^{2+} , the whole series of samples are formed at constant hole concentration; there should be no doping of holes onto the planes, yet the critical temperature T_c varies sharply across the series. Bond-valence-sum calculations ($r(\text{Pb}-\text{O}) \sim 2.0$ Å) indicate that, as regards crystal chemistry, Pb behaves as Pb^{IV} not Pb^{II} .

In this paper we present NMR, magnetic susceptibility (taken on a vibrating-sample magnetometer), and some structural data on four samples in the series; the characteristics of our samples are detailed in table 1 below.

Table 1.

Sample	Calcium x	T_c
Isis 2	0.2	0
Isis 3	0.3	19
Isis 4/O = 7.0	0.4	37
Isis 4/O = 7.1	0.4	0

Isis 2 and 3 both have oxygen contents of 7.0, having been quenched from 800 °C; there are however two Isis 4 samples, one which has been quenched from 800 °C with oxygen content 7.0, and the other which was quenched from 800 °C and then annealed for 16 hours at 400 °C in O_2 , giving an oxygen content of 7.1, and therefore is non-superconducting. (In subsequent discussion, if a sample is simply referred to as Isis 4, this means the O = 7.0 variant.) We have also synthesized an Isis 5 ($x = 0.5$) sample, and measured a T_c of 25 K. The Isis 4 composition therefore looks close to optimal doping, from which we might deduce that Isis 3 was underdoped, if we focus primarily on the Y/Ca ratio as the main determinant of the hole concentration of the planes.

We have performed NMR measurements on the yttrium and lead nuclei, measuring the spin-lattice relaxation, spin-spin relaxation, linewidth, and chemical/Knight shift as functions of temperature down to about 130 K from room temperature. A 1 mol l⁻¹ solution of YCl_3 has been used as a secondary reference for the yttrium measurements, and a $\text{Pb}(\text{NO}_3)_2$ solution as a secondary reference for the lead measurements. In general, very standard pulse techniques on a MSL Bruker 500 spectrometer were used for the experiments. The Meiboom-Gill [7] multi-pulse sequence, $90_0-\tau-180_{90}-2\tau-180_{90}-2\tau \dots$, was used for the measurement of the spin-spin relaxation. The ^{89}Y nucleus was chosen as a known probe of Cu-O-plane behaviour, whilst the ^{207}Pb nucleus should provide information about the charge reservoir away from the plane.

2. Results

The high-temperature (T') structural instability is small in this series and situated at about $T' \sim 180$ K, figure 1, showing unit-cell parameters obtained from neutron diffraction data [5]. There is little or no evidence of any associated magnetic effect in the bulk susceptibility

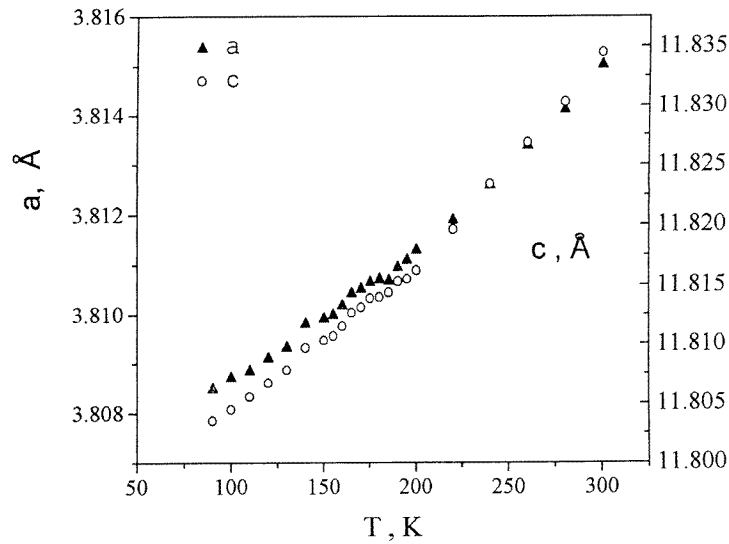


Figure 1. Structural behaviour with temperature; these are neutron diffraction data, showing *a*- and *c*-axis lengths for the sample Isis 3.

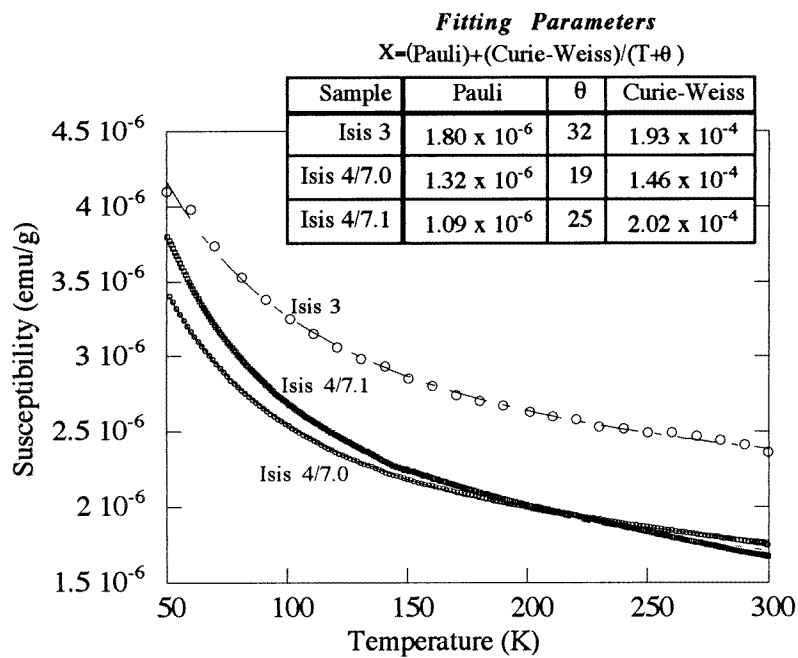


Figure 2. The susceptibility data, plotted over a restricted temperature range, in order to keep clear of superconductivity effects. All of the data were taken at a field of 1 T.

data, figure 2. The fits to the raw data, breaking the susceptibility into temperature-independent (Pauli) and Curie-Weiss components, are good, with correlation coefficients of 0.999; the fit lines are plotted in figure 2, but in the case of Isis 4/7.0 and 4/7.1 samples

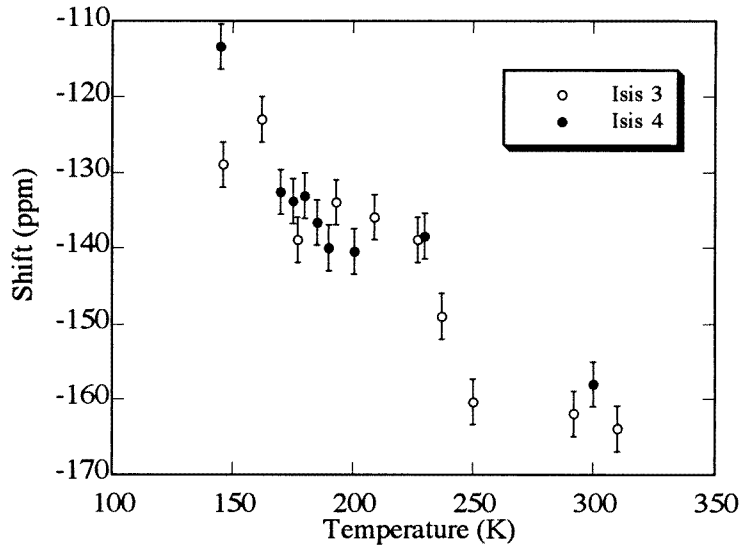


Figure 3. The ^{89}Y NMR results for the shifts in Isis 3 and 4.

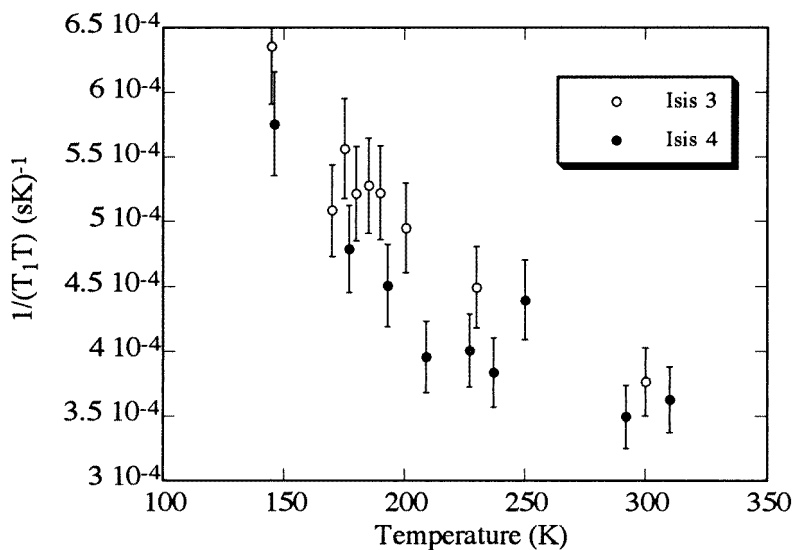


Figure 4. The ^{89}Y NMR results for the inverse of the product of the spin-lattice relaxation time T_1 and the absolute temperature T in Isis 3 and 4.

the density of experimental data points obscures these lines almost completely since the fit lines superimpose directly on top of the data points. The fitting procedure would predict error bars on the θ -values of about 3%, about 5% on the values of the Pauli term, and about 2% on the values of the Curie-Weiss term.

The trends with temperature for the NMR shift, spin-lattice relaxation rate $(T_1 T)^{-1}$ and linewidth for ^{89}Y in the $x = 0.4$ and $x = 0.3$ samples are illustrated in figures 3, 4, and 5, respectively. (The ^{89}Y signals for Isis 2 proved to be rather too weak to take the multiple

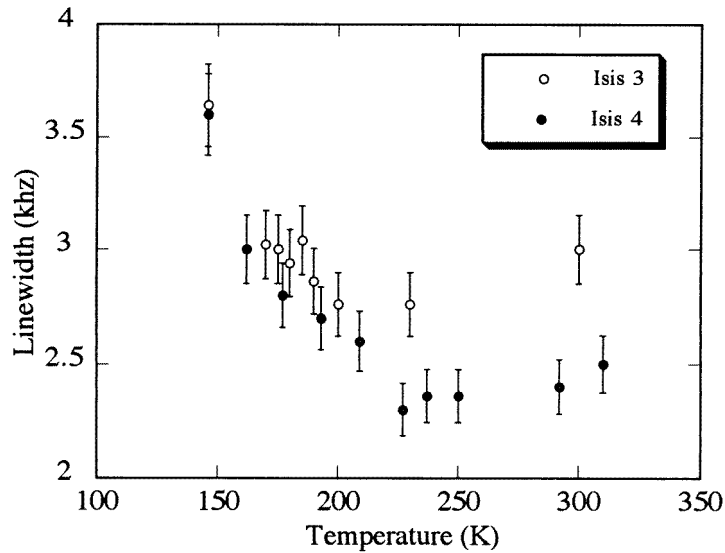


Figure 5. The ^{89}Y NMR results for the linewidths as a function of temperature.

values required to produce a plot as a function of temperature; this may indicate that this particular sample is magnetic at room temperature. No yttrium shift data were taken on Isis 4/7.1 because of time constraints.)

In figure 3, with shifts referenced to a zero at +200 ppm relative to the shift of a 1 M solution of YCl_3 , both Isis 3 and 4 samples show the ^{89}Y shift reducing in magnitude with temperature [8]. (This value of +200 ppm is an estimate of the zero of shift in these high- T_c systems [8].) In both samples the shift is negative and small, with a value at room temperature of -165 ppm moving to about -100 ppm as the temperature descends to 100 K. The ^{89}Y spin-lattice relaxation rate, figure 4, exhibits a weak temperature dependence in both Isis 3 and Isis 4. Discussed in the context of the decreasing magnitude of the shift as T descends in figure 3, these temperature dependences are surprising; in a normal metal with constant shift, T_1T is also a constant, so, if the shift gets smaller numerically, $(T_1T)^{-1}$ might be expected to get smaller as T descends. In both cases, experimentally $(T_1T)^{-1}$ becomes larger.

The narrowing of the linewidth as the temperature descends at higher temperatures in figure 5, certainly in Isis 4, may be connected with the effects shown in figures 6 and 7. In figure 6 the result of a Meiboom-Gill spin-echo measurement of T_2 is shown, where the spin-echo peak maxima are plotted as a function of time from the first 90° pulse. A clear oscillation is evident. This is unusual in these types of system; in many investigations on similar materials we have never before observed such effects. The oscillation frequency is plotted in figure 7 for three samples as a function of temperature. Such behaviour is taken to be the signature of a small spin-spin interaction between two unlike ^{89}Y sites [9, 10]. In Isis 4 this oscillation frequency, which measures the spin-spin splitting, is seen to decrease as the temperature is lowered, and this decrease may be the driving mechanism for the linewidth decrease observed in the high-temperature range in figure 5 for these samples. The forms of the oscillation observed in the Meiboom-Gill spin-echo decays in these samples are characteristic of a spin-spin interaction between two yttrium nuclei; only pairwise interactions will lead to such spectra [9, 10]. Because spin-spin splittings

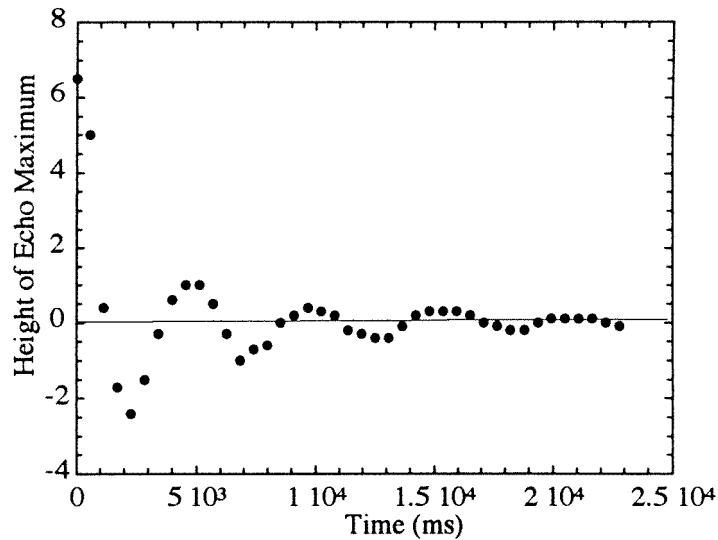


Figure 6. The characteristic form of the multi-pulse spin-echo decay. The graph plots the echo maxima. This particular signal came from the Isis 4 sample at 130 K. The time between 180° pulses was $570 \mu\text{s}$.

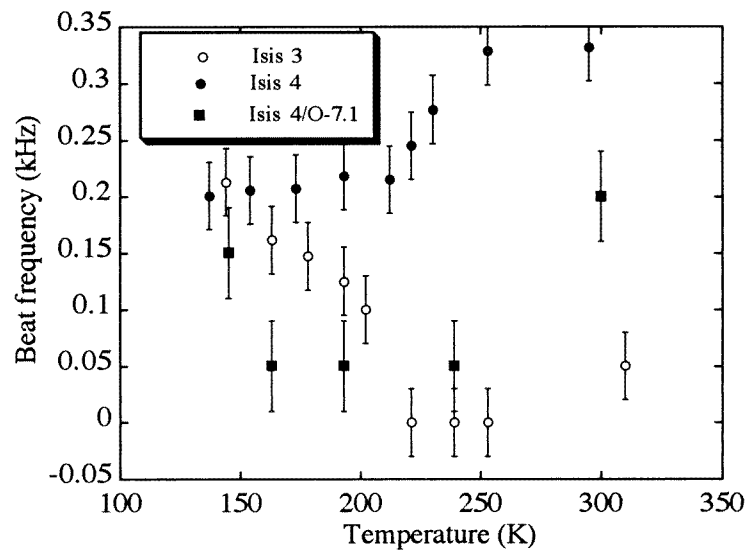


Figure 7. The oscillation frequency, taken from spectra such as figure 7, plotted as a function of temperature for three samples.

are unobservable between equivalent nuclei in spin-echo NMR, these two yttrium nuclei need to be 'unlike' [9, 10]. The statistical distribution of Y/Ca occupancy of the site will lead to differing shifts at different Y sites, so satisfying this condition [11]. However, the dimerization condition imposed by the appearance of the spectra in figure 6 is quite separate; yttrium nuclei must be interacting with each other in pairs, probably via the Cu–O conducting plane. The data in figure 7 indicate that this spin–spin coupling is a strong

function of temperature, certainly in Isis 3 and 4, but less convincingly so in the non-superconductor Isis 4/O = 7.1; 250 K appears to be an onset transition temperature. The different signs of the temperature coefficient for this oscillation frequency, figure 7, for Isis 3 and 4, are a puzzle.

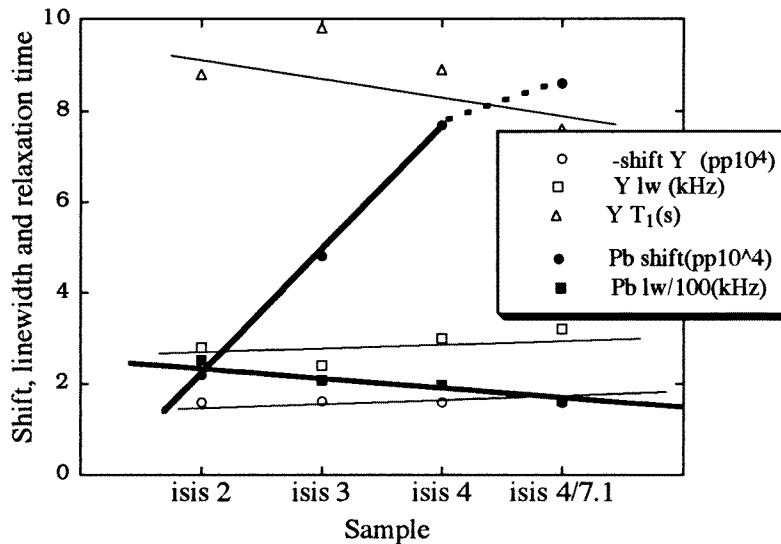


Figure 8. The ^{89}Y shift, linewidth and T_1 , as well as shift and linewidth data for ^{207}Pb , compared at room temperature for the four samples. The lines (bolder for Pb) are guides to the eye; for the Pb shift case the line has been broken in going from Isis 4/7.0 to 4/7.1 since this sample change corresponds to putting extra oxygen into the vicinity of the Pb.

Figure 8 shows the trend in room temperature data for all of the four samples of $\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2}\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{7+\delta}$ investigated, starting on the left with $x = 0.2$ in the formula unit, and ending up on the right with $x = 0.4$, and with an oxygen content in the formula unit of 7.1, in probably an overdoped state. Clearly the number of holes, a strong determinant of the critical temperature for superconductivity in these systems, has little or no influence on the particular ^{89}Y NMR parameters, at least at room temperature. Since hole density is also a determinant of magnetic state, and figure 2 demonstrates considerable variation of susceptibility across the formula series, it either appears that the magnetic state of the Cu spins has little influence on the yttrium NMR at room temperature or that the Cu spins form only a minor component of the total susceptibility.

We have measured the Pb spin-echo signal in Isis 4 at temperatures down to 160 K, finding a broad resonance, using a step-by-step frequency technique, of about 160 kHz at room temperature, broadening to 250 kHz at 160 K. The line maximum is independent of temperature and is at 104.400 MHz in our spectrometer. A reference sample of $\text{Pb}(\text{NO}_3)_2$ solution resonates at 104.320 MHz in the same field, and PbCl_4 would therefore resonate at 104.570 MHz. The absence of any temperature variation in the position of this line, in a range where the yttrium shift is changing markedly (figure 3), leads us to suppose that the Pb resonance is disconnected from the magnetic behaviour of the Cu–O planes. Room temperature shift data on all of the Pb resonances have been added to figure 8, showing a pronounced variation of the shift across the sample range at room temperature. (In this plot the shifts are referenced with respect to a lead nitrate solution.)

3. Discussion

Our first observation on the magnetic data, figure 2, is that there does not appear to be any magnetic anomaly around the temperature of the structural anomaly at 180 K in figure 1. Secondly, we note from the fitting described in figure 2, where we have kept to temperatures higher than 50 K in order to treat all of the samples on the same basis and to keep well clear of any superconducting transitions, that there is a temperature-independent (Pauli) and a Curie–Weiss term for each of the samples; the values of the fitting parameters are listed in the inset to the figure. The planar susceptibilities for YBCO quoted by Alloul *et al* [12] lie in the range 1 to 4×10^{-7} emu g⁻¹, substantially smaller than our measurements, and the temperature variation of these YBCO susceptibilities is such that the susceptibility grows with temperature. Thus the fitting procedure yields large values for the temperature-independent susceptibility component; furthermore the values listed in the inset to figure 2 for the Curie–Weiss component correspond to between 25 and 35% of the formula units in the samples carrying a moment of 1 Bohr magneton. This Curie–Weiss value is too large to be explained as due to impurity effects; it is likely to be due to the Cu ions on the Pb sites, whose fraction per formula unit is 35% for Isis 3 and 30% for Isis 4. The values of θ listed in the inset to figure 3 indicate weak antiferromagnetic correlations between these local moments. The variation of the Pauli term across the sample series is unexpected; as one progresses from Isis 3 to Isis 4/7.0 to Isis 4/7.1, hole doping on the planes would be expected to dampen the antiferromagnetic correlations on the conducting planes and thus lead to an increase in the temperature-independent term. There does not appear to be any correlation between the observed yttrium shifts and the fitted Pauli contributions.

Comparing figures 3 and 4, the yttrium shift and relaxation rate data, the similarity in trend over the temperature range is striking. This leads us to favour the idea that the trend in the shift as the temperature goes down is driven by an increase in a (smaller-magnitude) positive shift contribution; this is a well-known effect in transition metal NMR and would lead, at the same time, to a decrease in the net magnitude of the shift and to a rise in the relaxation rate product $(T_1 T)^{-1}$, since the shift/relaxation rates from the two contributions would subtract/add. In looking at the trend in the relaxation we are also reminded of the well-known ‘spin-gap’ effects observed in the high-temperature superconductors, although this is usually a signature of underdoping.

Figure 5 appears to demonstrate strong broadening at low temperature in both samples, but significantly both also show a line narrowing as T descends in the range from 300 to 250 K. The narrowing is just significant, but the difference in width between Isis 4 and Isis 3 in this temperature range is marked. Both samples exhibit ⁸⁹Y NMR widths considerably broader than widths observed, say, in stoichiometric YBCO, where 1 kHz or less is common. We may safely assume that the larger widths in Isis 3 and 4 are associated with a distribution of Knight shifts, due to a range of local environments stemming from the random nature of the Pb/Cu and Y/Ca substitutions. The decreased width of Isis 4 in the high-temperature range would therefore indicate a more ordered structure. At lower temperatures the widths in the two samples equalize, which may indicate similar numbers of paramagnetic centres in the samples.

There is some interest in comparing our results [13, 14] for ⁸⁹Y NMR in the Tl/Pb 1212 material with the present results, figure 3, for the Cu/Pb 1212 material. To summarize the comparison:

(i) the trends in the shift with temperature [13, 14] are comparable to those shown in figure 4;

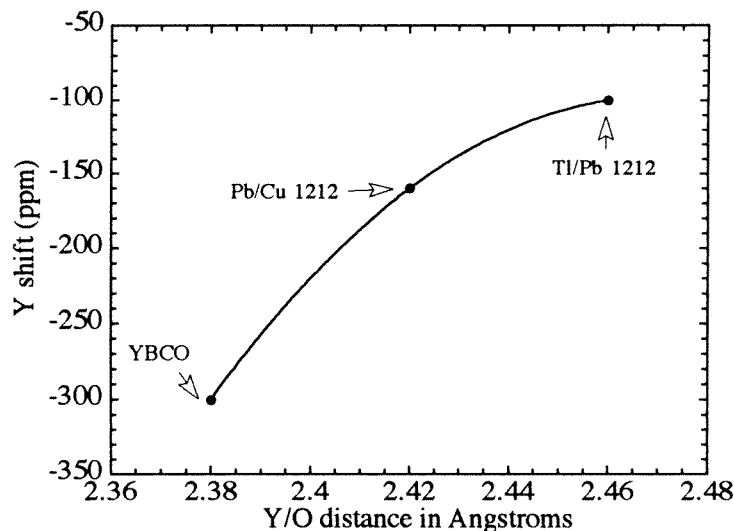


Figure 9. Yttrium shifts at room temperature in three materials, plotted against the yttrium-planar oxygen distance. The y-axis units are relative to the accepted Y origin of shift of +200 ppm with respect to a 1 M solution of YCl_3 .

(ii) the ^{89}Y shifts are numerically even smaller in Tl/Pb than in Cu/Pb; e.g. in the Cu/Pb system at room temperature we have shifts of about -160 ppm relative to the accepted zero of shift of +200 ppm with respect to yttrium trichloride, whereas in the Tl/Pb system the room temperature shifts are around -100 ppm relative to the same reference; and

(iii) in the Tl/Pb system, where one can observe the yttrium NMR in the optimum to underdoped regions by varying the yttrium concentration, there is not much change in yttrium shift behaviour or magnitude with doping; figure 3 similarly exhibits much the same behaviour for the two samples, and figure 8 reinforces this point over a wider range of samples.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ shows yttrium shifts of much larger magnitude than either of these two 1212 materials. A simple explanation of the general magnitude of the yttrium shifts may be sought in comparing shifts at optimal doping for the Tl/Pb, Cu/Pb, and YBCO systems with the distance between the yttrium and planar oxygen; see figure 9. This simple monotonic behaviour with distance would appear to indicate that the variation of the yttrium shift in the three systems stems from a variation of the hyperfine coupling constant linking the yttrium to the magnetic planes, rather than through any variation of the planar susceptibility from system to system. Given the idea advanced earlier that the shifts observed may be composite shifts, involving both positive and negative counterbalancing contributions, then the trends observed in figure 9 may reflect the variation of the proportions of these partially cancelling factors as the distance between the yttrium and the planar oxygens varies.

In assessing the potential link between the local magnetic NMR data in figures 3, 4, 5, 6, and 7, and the structural anomaly of figure 1, it has to be said that the NMR does not produce, within the errors associated with the technique, any convincing evidence for a link between magnetic and structural properties at around 180 K. There is NMR evidence for the onset of a structural event at around 250 K, as shown particularly in the Meiboom-Gill splittings of figures 6 and 7. This may be the high-temperature local precursor of the

long-range order characterized in figure 1 at 180 K.

As stated earlier, the appearance of this oscillation in the spin-echo decay indicates that a significant fraction, at least 20%, of yttrium nuclei form dimers. This estimate originates from an approximate fit of the spectra of the type shown in figure 6 into (i) decaying, and (ii) oscillating and decaying components, where the dimers would correspond to component (ii). We have performed a number of careful neutron, x-ray and resonance x-ray diffraction experiments, and we also observe an anomaly associated with the yttrium site. For the $x = 0$ end member the yttrium site refines normally; however, when some calcium substitution occurs, i.e. $x > 0$, anomalous ITF (isotropic temperature factors) are obtained. Allowing the yttrium site to split, with atoms moving slightly off the ideal site in the z -direction (by about 0.001 nm), restores the stability of the site. This indicates a slight distortion of the yttrium site for $x > 0$, and we speculate that the origin of the dimerization effect observed via NMR may lie in this small movement of the yttrium nucleus away from the cell centre position. Along a line of yttrium nuclei in between two copper oxide planes we would envisage one yttrium nucleus equi-spaced from the two planes, one above and one below, with its nearest-neighbour yttrium being displaced upwards, say, towards the upper copper oxide plane. These two yttrium nuclei are thus inequivalent because of their different distances from the copper oxide planes, and their spin–spin coupling can thus be revealed in the NMR experiment. A question that then arises is why any two yttrium nuclei can appear separate from their other yttrium nearest neighbours; it may be that this could arise because the dimerization involves one of the ‘dimered’ yttrium nuclei being surrounded by three calcium nuclei in the other nearest-neighbour Y positions.

Suter *et al* [4] speculate that the driving cause of the variations in the NMR/NQR parameters that they observe in the 124 YBCO system at around 180 K is a charge-density-wave instability, causing a transfer of holes between chain and plane, and setting off fluctuation effects; they discount any structural cause. The evidence in our system is similar, and we have good corroboration that associated structural effects, such as the dimerization of the yttriums, are very weak [5]. We agree then that we are probably observing an electronic effect. In our case the sharpest feature is the effect on the spin–spin coupling. It is clear that the beginnings of a charge-density-wave instability could affect the nearest-neighbour J -couplings between yttrium nuclei, but other explanations may well be more suitable.

Finally we look at the Pb NMR and compare our results, for yttrium and lead, with those for the 1212 system, $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ [13–15]. In the system $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$, where resonances up to 104.7 MHz were observed, the shifts varied with yttrium concentration in just the same way as did the shift of the ^{63}Cu ; we may assume that the Pb resonance in this case ‘senses’ the Cu–O-plane magnetization. The origin of the shifts [15] in the thallium-based 1212 system is 104.47 MHz, rather nearer Pb^{4+} (104.57) than Pb^{2+} (104.32). In our Cu/Pb-based 1212 system, since there is no shift with temperature in Isis 4, we may take the Pb resonance positions as chemical shifts. Thus from this room temperature Pb NMR data there are indications:

(1) that there is a systematic trend in the Pb shift across the series of compounds in the 1212(Pb/Cu) system; we might be tempted to associate this trend of the shift with a trend of the Pb valence, in which case, in a linear model, we ascribe Pb valences of 2.2^+ , 2.4^+ , 2.6^+ and 2.7^+ to Isis 2, 3, 4 and 4/7.1 respectively; and

(2) that Pb in the 1212 system based on Tl is closer to Pb^{4+} than Pb in the 1212 system based on Cu.

In indication (1) above, it is important to realize that the absolute values of the Pb shifts are affected by factors other than valence; Pb–O bond lengths, valence sum calculations and

x-ray absorption experiments all indicate that the Pb valence is close to 4. Thus the trends in valence indicated by the NMR shift data are more important than the absolute values of that valence. In this context it is particularly interesting to note that the relative shift on oxidation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, from 7.0 to 7.1, corresponds to a small upward change of oxidation state of Pb, when 0.2 electrons would nominally be extracted from the cations to accommodate the uptake of 0.1 oxygen; one would have expected the reservoir holes to be associated with the Cu and/or the O atoms, rather than with the Pb atoms. Any more definitive conclusion here would require an extended set of measurements of chemical shifts in lead salts to establish firmly any connection between chemical shifts and the valence state of lead.

4. Conclusions

In seeking evidence that the small anomaly observed in the structural parameters of a 1212 Pb/Cu-based superconductor might be electronically driven we were not able to produce any convincing support from either magnetic or NMR experiments. We have however discovered an anomaly in the NMR at a higher temperature; we speculate that this effect may be a local precursor of the structural anomaly and is associated with yttrium–yttrium dimerization. This is not inconsistent with others' hypothesis [4] that a charge-density-wave is involved at around these temperatures in related systems. There is some indication that the Pb valence state in the 1212 Pb/Cu alloy series varies across the series. Adding further oxygen apparently adds holes to the Pb system, as well as to the Cu/O system.

A comparison of the yttrium NMR response in this 1212 Pb/Cu, in 1212 Tl/Cu and in stoichiometric YBCO has shown up a correlation of these magnetic data with known structural data, in particular with yttrium–oxygen distances.

Acknowledgments

We thank the Royal Society for providing funds to enable one of us (SGT) to spend three months in St Andrews, on leave from Institute of Metallurgy in Ekaterinburg, during which time many of these measurements were undertaken. The Nuffield Foundation are also thanked for a Science Research Fellowship (JTSI). The susceptibility data were taken on the St Andrews vibrating-sample magnetometer; we thank Professor R Cywinski for making this available and Adrian Hillier for valuable assistance in running the magnetometer

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