NMR studies of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$

S M DOYLE, R DUPREE*, A P HOWES, D McK PAUL and
M E SMITH†

Physics Department, University of Warwick, Coventry CV4 7AL, U.K. †Bruker Analytische
Messtechnik GmbH, Silbersteinen. D-7512, Rheinstetten 4, W. Germany

Abstract. Copper NMR has been studied as a function of temperature in a number of superconducting $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ samples. The electric field gradient is very small and the Knight shift is 2380 ppm at room temperature, both of these implying that the copper is in a Cu^+ state. The Knight shift decreases with temperature particularly below T_c . The spin contribution to the Knight shift is estimated to be ~ 200 ppm (about a factor ten smaller than in $\text{YBa}_2\text{Cu}_3\text{O}_7$) indicating that $N_s(E_F)$ at the copper sites is small in this material.

Keywords. NMR; Nd–Ce–CuO₄; Knight shift.

1. Introduction

There has been much interest in the electron doped (*n*-type) oxide superconductors such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, since their discovery earlier this year (Tokura *et al* 1989). The parent compound $\text{Nd}_2\text{CuO}_{4-y}$ is antiferromagnetic and superconductivity appears abruptly for a concentration of cerium near $x \sim 0.15$. The two-dimensional sheets of Cu–O squares are clearly important for the superconductivity and whilst there is no generally accepted theory of the pairing mechanism in the oxide superconductors, as pointed out by Rice (1989), the electron-doped compounds are a more clear-cut example of materials where the *t*–*J* model should be applicable and thus their study is of considerable importance.

In this work Cu NMR is used as a microscopic probe of the electronic behaviour of some $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ samples with *x* near 0.15. Two previous reports of NMR in this system have appeared (Zheng *et al* 1989; Abe *et al* 1989). Both have been mainly concerned with low temperature investigations particularly to look for magnetic order in the superconducting samples. However they both reported a relatively small electric field gradient at the copper site and a small positive shift at 30 K.

2. Experimental

The samples were prepared by mixing stoichiometric quantities of the oxides and reacting these at 950°C for about one week with repeated regrindings. They were then pelletized and sintered overnight in air at 1150°C before annealing at 1050°C for about 24 h in argon. X-ray diffraction showed that the materials were single phase. T_c was measured using a.c. susceptibility and for the superconducting sample discussed below T_c was ~ 21 K. NMR measurements were carried out on a Bruker MSL360 and

---

*For correspondence

MSL200 operating at ~ 96 MHz and 53 MHz respectively. The temperature was varied using a Bruker gas flow system. For the wider ^{63}Cu lines a spin echo ($90\text{-}\tau\text{-}180$) sequence was used with pulse lengths of $1.8\text{ }\mu\text{s}$ and $3.6\text{ }\mu\text{s}$ and a delay of $35\text{ }\mu\text{s}$ and the line shape determined from a point by point measurement every ~ 100 kHz Fourier transforming from the peak of the echo. For the narrow ^{63}Cu lines the free induction decay signal was acquired using a $3\text{ }\mu\text{s}$ pulse and then Fourier-transformed to give the signal.

3. Results

Figure 1 shows a typical lineshape at room temperature. The line is relatively narrow (~ 1 MHz) and shows no evidence for any quadrupolar effects on the lineshape unlike ^{63}Cu in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (see e.g. Mehring 1989). This is in agreement with the low temperature results of Zheng *et al* (1989) and Abe *et al* (1989). One sample gave a much narrower line and this is shown in figure 2 as a function of temperature together with the line from copper metal. It can be seen that at room temperature the ^{63}Cu in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is very similar both in position and width to copper metal. In fact it was only after the sample was investigated in a copper-free probe as a function of temperature that we became completely convinced as to its veracity. The shift of this line is weakly dependent on temperature above T_c decreasing from 2380 ppm at 300 K to 2250 ppm at 25 K. It then decreases more rapidly to 2035 ppm at 7 K. At low temperatures a clear shoulder is visible on the line whose shift increases as the temperature drops. The spin lattice relaxation time T_1 was found to be independent of temperature and to be ~ 1.5 ms.

4. Discussion

The width of the line shown in figure 1 is ~ 5 times the linewidth observed by Abe *et al* in a field of 10.8 kG indicating that the major cause of linewidth in this sample is inhomogeneous broadening since any quadrupolar contribution to the linewidth would be smaller at our higher field. Thus in agreement with them we find that in

Figure 1. Typical lineshape for ^{63}Cu in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ at room temperature.

Figure 2. ^{63}Cu spectra at various temperatures for samples giving narrowest ^{63}Cu line.

superconducting samples there can only be a very small electric field gradient at the copper sites. This is unexpected since the local symmetry is not cubic and in NdCuO_4 the zero-field spectra correspond to an electric field gradient of 28 MHz for ^{63}Cu (Abe *et al* 1989).

The electric field gradient must be reduced significantly by a combination of shielding from the conduction electrons present and from a change in the local configuration of some of the Cu ions from $3d^9$ to $3d^{10}$ as suggested by Tranquada *et al* (1989). This change in the local configuration is also suggested by the spectra shown in figure 2. The inhomogeneous broadening observed for the sample shown in figure 1 could be caused by the distribution of local fields present from the local moments on the Nd ions or it could possibly be due to chemical shift or Knight shift anisotropy in our powder samples. However this latter possibility seems very unlikely since the anisotropy would have to be much larger than in $\text{YBa}_2\text{Cu}_3\text{O}_7$ even though the electric field gradient at the copper site is at least two orders of magnitude smaller; furthermore the ^{63}Cu line shows no evidence of the characteristic lineshape expected for the case of axial anisotropy.

The narrow line observed for the sample shown in figure 2 could be from a fortuitously aligned sample, however attempts to align $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ in the same

Figure 3a. Shift and temperature of the ^{63}Cu line in figure 2. $\blacklozenge$ narrow line, $\square$ shoulder.

Figure 3b. Shift vs $1/T$ for the "shoulder" of the spectra shown in figure 2.

way as has been successfully done for $\text{YBa}_2\text{Cu}_3\text{O}_7$ were only partially successful and did not lead to the linewidth reduction observed in figure 2. The most likely cause of the narrow linewidth is therefore a more homogeneous sample with a fairly ordered arrangement of Nd and Ce ions around the copper atoms.

The shift of the line at room temperature, 2380 ppm, is only a few ppm less than copper metal, however it decreases quite rapidly with temperature particularly below T_c . The shift vs temperature is shown in figure 3a together with the shift of the shoulder on the resonance which is visible below ~ 100 K. The observed Knight shift K is the sum of spin and orbital contributions i.e. $K = K_s + K_{\text{orb}}$ each of which is proportional to its susceptibility χ_s and χ_{orb} . The orbital susceptibility and thus K_{orb} is not affected by the superconducting transition and the temperature dependence of K should be associated with K_s . Although the shift decreases more rapidly below T_c it does not follow a Yosida-type function such as is observed for spin-pairing in a BCS superconductor like aluminium. Because of demagnetizing effects it is difficult to estimate the magnitude of the field in the superconductor well below T_c . Nevertheless some idea of the magnitude of K_s can be made from the change in shift between say 25 K

and 7 K, we find that $K_s \approx 220$ ppm and $K_{\text{orb}} \sim 2000$ ppm. This can be compared with an isotropic value of K_s of 2000 ± 200 ppm for the Cu planes in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Barrett *et al* 1990). The much smaller value for this shift implies a lower density of states at the Fermi level in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ consistent with the lower T_c . Although K_{orb} is considerably less than for $\text{YBa}_2\text{Cu}_3\text{O}_7$ where $K_{\text{orb}} \parallel c$ is 1.28% and $K_{\text{orb}} \perp c$ is 0.28% (Barrett *et al* 1990) it is still relatively large. However, for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ we do not feel it arises from an anisotropic $3d^9$ configuration (there is little evidence for anisotropy in the spectra) but from a band situation where

$$K_{\text{orb}} \approx \beta \frac{n_i n_F}{\Delta} \leftarrow \frac{1}{r^3},$$

(n_i and n_F are the number of occupied and unoccupied Bloch states, Δ is the conduction bandwidth and β the Bohr magneton) (Clogston *et al* 1964). Using this relationship with $n_i = 9.73$, $n_F = 0.27$, Walstedt and Yafet (1974) showed that K_{orb} for copper metal can be as large as 2500 ppm although the most likely value was 600 ppm. For $\text{Nd}_{1.85}\text{Ce}_{1.15}\text{CuO}_4$ $n_i n_F$ will be ~ 3 times larger than for Cu metal giving $K_{\text{orb}} \sim 1800$ ppm (for the same Δ), very close to our experimental value.

Figure 3b shows the shift of the shoulder and the main peak vs $1/T$. The temperature dependence of the shoulder can be well approximated by a Curie Law dependence suggesting that it follows the susceptibility of the Nd moments. It is likely that this line comes from parts of the sample which are not superconducting (the Meissner fraction for this sample was 20%).

5. Conclusions

The width of the ^{63}Cu line together with its relatively small anisotropy imply that the copper observed in these NMR experiments is in a $3d^{10}$ configuration. There is only a small spin contribution to the Knight shift indicating that $N_s(E_F)$ at the copper sites is low.

Acknowledgement

We wish to thank SERC for their support.

References

- Abe M, Kumagi K, Awaji S and Fujita T 1989 *Physica* **C160** 8
- Barrett S E, Durand D J, Pennington C H, Slichter C P, Friedman T A, Rice J P and Ginsberg D M 1990 *Phys. Rev.* **B41** 6283
- Clogston A M, Jaccarino V and Yafet Y 1964 *Phys. Rev.* **A134** 650
- Mehring M 1989 *IBM J. Res. Dev.* **33** 342
- Rice T M 1989 *Nature (London)* **337** 686
- Tokura Y, Takagi H and Uchida S 1989 *Nature (London)* **337** 345
- Tranquada J M, Heald S M, Moodenbaugh A R, Liang G and Croft M 1989 *Nature (London)* **337** 720
- Walstedt R E and Yafet Y 1974 *Solid State Commun.* **15** 1855
- Zheng G, Kitaoka Y, Oda Y and Asayamu K 1989 *J. Phys. Soc. Jpn.* **58** 1910