The continued absence of EPR at high temperatures in $Ln_2Cu_{1-x}Zn_xO_4$ (Ln=La,Nd)

1994 J. Phys.: Condens. Matter 6 L315

(http://iopscience.iop.org/0953-8984/6/21/006)

J. Phys.: Condens. Matter 6 (1994) L315–L318. Printed in the UK

LETTER TO THE EDITOR

The continued absence of EPR at high temperatures in $Ln_2Cu_{1-x}Zn_xO_4$ (Ln = La, Nd)

R Janes† and P P Edwards‡

† Department of Chemistry, Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK
‡ School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK

Received 17 March 1994

Abstract. EPR measurements were carried out up to 423 K for the series $Nd_2Cu_{1-x}Zn_xO_4$ ($x = 0.00$–0.20) and $La_2Cu_{1-x}Zn_xO_4$ ($x = 0.00$–0.10). Despite the drastically reduced 2D antiferromagnetic spin-correlation lengths, brought about by both Zn doping and elevated measurement temperatures, no intrinsic EPR signals have been detected from these materials.

A common feature of all high-T_c superconducting cuprates and their insulating 'parent' compounds is the existence of highly polarizible CuO layers within a lamellar structure, and the nature of the magnetic interactions within these sheets is thought to be crucial to the mechanism of superconductivity [1]. Although the Cu ions are nominally in the divalent state ($3d^9$) with a single hole in the $d_{x^2-y^2}$ orbital, materials such as La_2CuO_4 and Nd_2CuO_4 (progenitors of the superconducting phases $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_{4-\delta}$ respectively) are characterized by the absence of intrinsic Cu^{2+} electron paramagnetic resonance (EPR) signals at temperatures well above their three-dimensional (3D) antiferromagnetic ordering temperature [2, 3]. Indeed, no EPR signals for La_2CuO_4 [2] or R_2CuO_4 (R=Pr, Nd, Sm, Eu or Gd) [3] were detected up to $\sim$ 600 K, these systems having Néel temperature (T_N) values around 270 K. Furthermore, a recent investigation by Simon and co-workers [4] has demonstrated the absence of a Cu^{2+} EPR signal up to 1150 K in single crystals and ceramic pellets of $La_2CuO_{4+\delta}$. This response, together with low magnetic susceptibilities, was found to be common to cuprates possessing long-range 180° Cu–O–Cu interactions [5]; the fundamental importance of antiferromagnetism in the undoped CuO_2 sheets has been highlighted by Muller [6]. Wubbeler and Schirmer [7] have recently reported the detection of strong resonances from samples of $La_2CuO_{4+\delta}$, which were attributed to small spin-polarized ferromagnetic clusters within an antiferromagnetic matrix, containing at least five Cu^{2+} ions coupled by virtue of sharing a single O hole. The thermal behaviour of these units was in accord with the existence of localized 'magnetic polarons' and their role as pecursors to the superconductivity where they exist in a percolated state.

The magnetic behaviour of systems such as $La_{2-x}Sr_xCuO_4$ has been modelled on the basis of CuO layers containing antiferromagnetically coupled Cu moments, arising from superexchange via intervening O p orbitals. From neutron-scattering data, Shirane and co-workers [8] observed that at room temperature, although there is no long-range two-dimensional (2D) ordering (a consequence of the Hohenberg–Mermin–Wagner theorem for a 2D Heisenberg antiferromagnet [9, 10], the instantaneous 2D spin correlation length exceeds

0953-8984/94/210315+04$19.50

200 Å within the plane with an exchange constant $J \simeq 1500$ K. The transition to the 3D ordered Néel state is driven by the relatively weak interplanar coupling $J_\perp$ ($J_\perp \simeq 10^{-5} J$) when the interplanar exchange energy exceeds the thermal fluctuations of the lattice. Above T_N the interplanar coupling has very little influence on the antiferromagnetic spin fluctuations in the planes.

Clearly these strong exchange interactions within the CuO planes will form coupled energy levels of the constituent metal ions and will profoundly influence the EPR response of these systems. Chakravarty and Orbach have suggested that the anisotropic exchange terms severely broaden the EPR signals in La_2CuO_4 [11]. Given that the linewidth scales as $(\xi/a)^3$ where a is the lattice constant and ξ the 2D spin-correlation length, a linewidth of 190 kG at 380 K was calculated, which falls to 13 kG at 500 K. In addition, we would expect to effect a substantial reduction in the correlation length by site-specific substitution of magnetic or non-magnetic ions at the Cu sites; Zn^{2+} as a substituted ion is particularly suitable for study, as, due to their similar ionic radii, we would expect Zn^{2+} to substitute in a random fashion onto the Cu sublattice. In this regard, Chakraborty and co-workers have reported DC magnetization data for the $La_2Cu_{1-x}Zn_xO_{4-y}$ system that showed a progressive suppression of the Néel temperature from $T_N = 240$ K to 135 K when $x = 0.00$ and 0.03 respectively [12]. It was proposed that the precipitous decrease in T_N arose from disorder-induced reduction in the 2D correlation length, rather than any fundamental modification of the interplanar exchange term.

We have previously reported the lack of an intrinsic EPR signal in the materials $La_2Cu_{1-x}Zn_xO_4$ and $Nd_2Cu_{1-x}Zn_xO_4$ at ambient temperature [13] and, in view of recent reports [4, 7], have extended this to further optimize our measurement conditions (i.e. reducing ξ_{2D} to the absolute minimum) by the simultaneous approach of both *maximizing the* Zn^{2+} *substitutional level*, and carrying out EPR studies at *elevated temperatures*, such that $T \gg T_N$.

Samples of $Nd_2Cu_{1-x}Zn_xO_4$ (x = 0.00–0.10) and $La_2Cu_{1-x}Zn_xO_4$ (x = 0.00–0.10) were prepared from stoichiometric amounts of Nd_2O_3, La_2O_3, CuO and ZnO. La_2O_3 was prefired at 950 °C. These mixtures were ground, pelletized and fired initially at 950 °C in an O_2 atmosphere, followed by a further anneal in O_2 at 1000 °C with several intermediate grindings and pressings. X-ray powder diffraction revealed all materials to be single phase up to a substitutional level of $x = 0.1$. As we have previously reported the ratio of lattice parameters c and a remains constant over the series, which is clearly strong evidence for random substitution of Zn^{2+} for Cu^{2+} with the materials having the essential crystallographic features of the parent phase.

EPR measurements were carried out between 300 K and 423 K using a Jeol JES-RE1X spectrometer. The latter was equipped with an N_2 compressor and an ES-DVT2-1 digital temperature controller to facilitate measurements at high temperatures. In all cases no EPR signals intrinsic to the bulk material were detected up to the highest temperature investigated. In many samples weak signals assigned to Cu^{2+}-containing impurity phases (present at levels far below the XRD detection limits) were observed. Typical signal amplitudes correspond to Cu^{2+} concentrations of $\sim 10^{14}$–10^{15} spins cm^{-3}. An example of this type of impurity signal is shown in figure 1, the intensity of which falls in a Curie-like manner with increasing temperature. Clearly the detection of such 'extrinsic' resonances at 423 K, and at a concentration below 10^{15} spins cm^{-3}, establishes the intrinsic observability of exchange-coupled Cu moments in these samples under our experimental configuration.

The data reported here are in contrast with previous EPR studies of 2D antiferromagnets, e.g. K_2MnF_4, where EPR signals were observed at measurement temperatures well in excess of T_N (the linewidth minimum being $\sim 2T_N$) in the paramagnetic regime [14]. An

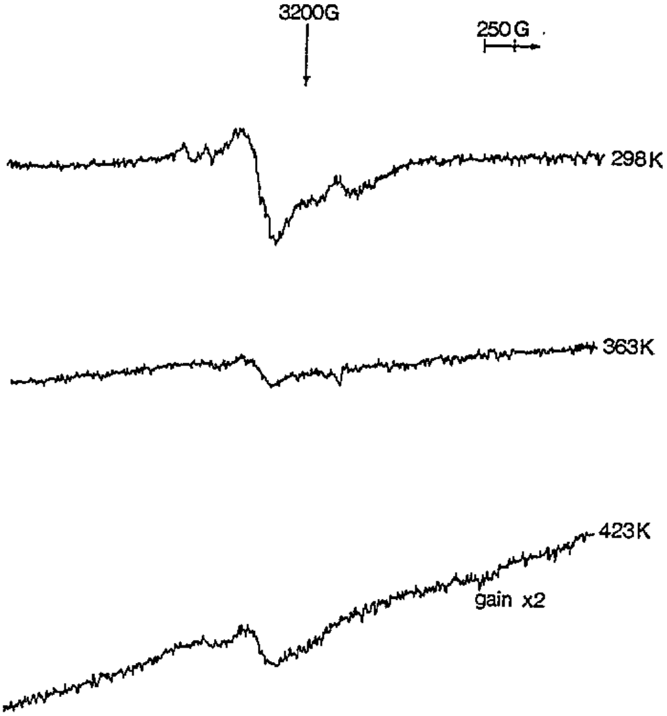

Figure 1. The first derivative X-band EPR spectrum for $Nd_2Cu_{0.90}Zn_{0.10}O_4$ measured at elevated temperatures, showing a weak resonance assigned to Cu^{2+}-containing impurities.

anomalous increase in linewidth is generally observed when the temperature is lowered towards T_N. As we have previously discussed the situation in the Zn-substituted cuprate samples reduces to that of a percolation problem in a similar manner to the well studied dilute 2D antiferromagnet $Rb_2Mn_xMg_{1-x}F_4$ [15]. This system also consists of strong nearest-neighbour antiferromagnetic interactions with only weak between-plane coupling. Neutron scattering has shown the Néel temperature of this system to fall by less than 1 K below the classical percolation threshold ($x = 0.59$); below this value the magnetic ions form clusters, which may be coupled by virtue of weak next-nearest-neighbour interaction; however, this interaction will not support long-range ordering. In addition, when $x < 0.59$ the correlation length was shown to increase with decreasing temperature, saturating at a point determined by the finite cluster size. The changes in spin dynamics as a function of x were reflected in the temperature dependence of EPR linewidth. Notably for $x \simeq 0.59$ at reduced temperatures, antiferromagnetic correlations lead to rapid line broadening with decreasing temperature.

The extent to which we can manipulate the magnetic properties of the Zn-substituted insulating cuprates studied here is determined by the solubility limits of the system. Clearly the Zn loading levels achieved here appeared not to be high enough to simply generate 'localized' Cu moments with no nearest-neighbour spin–spin interactions. However, if we consider one of the Zn^{2+}-substituted systems, e.g. $La_2Cu_{0.99}Zn_{0.01}O_4$, Chakraborty has reported a Néel temperature of 173 K, and clearly our measurements at higher temperature (at, and beyond, $2T_N$) did not reveal an EPR line, displaying a strongly temperature-dependent linewidth. Clearly, in the layered cuprates, the 2D precritical region, characterized by strong antiferromagnetic spin correlations, extends to temperatures far in excess of any of those observed for previously studied 2D antiferromagnets. In addition, it suggests that 'normal' spin-relaxation processes at these elevated temperatures are not sufficiently great to broaden lines beyond detection. Alternatively, we suggest a re-evaluation of the published correlation lengths for these materials may be necessary, in order to clarify this vexing problem.

References

[1] See, for example, Poole C P 1988 *Copper Oxide Superconductors* (New York: Wiley Interscience)

[2] Mehran F and Anderson P W 1989 *Solid State Commun.* 71 29

[3] Oseroff S B, Rao D, Wright F, Vier D C, Schultz S, Thompson J D, Fisk Z, Cheong S W, Hundley M F and Tovar M 1990 *Phys. Rev.* B **40** 1934

[4] Simon P, Bassat J M, Oseroff S B, Fisk Z, Cheong S W, Wattiaux A and Schultz S 1993 *Phys. Rev.* **48** 4216

[5] Shreedar K and Ganguly P 1988 *Inorg. Chem.* **27** 2261

[6] Muller K A 1993 *Mater. Chem. Phys.* **33** 171

[7] Wubbeler G and Schirmer O F 1992 *Phys. Status Solidi* b **174** K21

[8] Shirane G, Endoh Y, Birgeneau R, Kastner M A, Hidaka Y, Oda M, Suzuki M and Murakami T 1987 *Phys. Rev. Lett.* **59** 1613

[9] Hohenberg P C 1967 *Phys. Rev.* **158** 383

[10] Mermin N D and Wagner H 1966 *Phys. Rev. Lett.* **17** 1133

[11] Chakravarty S and Orbach R 1990 *Phys. Rev. Lett.* **64** 224

[12] Chakraborty A, Epstein A J, Jarrel M and McCarron E M 1989 *Phys. Rev.* B **40** 5296

[13] Janes R, Singh K K, Burnside S D and Edwards P P 1991 *Solid State Commun.* **79** 241

[14] Richards P M and Salamon M B 1974 *Phys. Rev.* B **9** 32

[15] Oseroff S B, Rao D, Wright F, Vier D C, Schultz S, Thompson J D, Fisk Z, Cheong S W, Hundley M F and Tovar M 1990 *Phys. Rev.* B **40** 1934