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Electron paramagnetic resonance studies in the oxides $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_y$

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Abstract. We have recently reported our results on magnetic susceptibility and microwave absorption studies on $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_y$ and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$. In the present work two important observations of these investigation, viz. the dependence of T_c on Gd-concentration and the absence of EPR-signals of Gd and Cu, are considered in greater detail. It is suggested that the microwave absorption by fluxon lattice might be playing one of the important and effective pathways for electron spin relaxation resulting in nonobservation of EPR signals.

Keywords. EPR; Gd-concentration; microwave absorption.

1. Introduction

Among the 123-type high temperature superconductors the Gd-compound $GdBa_2Cu_3O_{7-x}$ is of special interest due to the paramagnetic nature of Gd^{3+} which is known to retain its magnetic properties with Russell Saunders State of $^8S_{7/2}$. The speciality of this material is due to the well-known (Baberschkie 1976) pair-breaking effects of magnetic ions in superconductors. The occurrence of superconductivity in Gd-123, with T_c comparable to that of Y-123, established that Gd^{3+} (more generally, the RE^{3+} ions) do not have any role in the superconductivity and also that their interaction with superconducting carriers is insignificant if not completely absent. A number of EPR investigations have been attempted on Gd^{3+} in 123 compounds, the most recent being in a single crystal of $YBa_2Cu_3O_{6-y}$ by Shalteil *et al* (1989) (for other reports, see the references in this paper). These authors have shown that Gd-EPR gets exchange-narrowed and suggested that there exists a magnetic spin pairing around 110 K.

We (Sampathkumaran *et al* 1989) have recently investigated the Bi-based superconductors $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_y$ and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ by DC magnetic susceptibility (χ) and EPR studies. We have clearly established that a correlation exists between conventional χ-studies and changes in microwave absorption as the sample was cooled through T_c. Further, we have shown that the superconductivity is suppressed for high concentrations of Y and Gd. There are two important observations in our investigation which need further attention. These are: (i) depression of T_c with Gd/Y concentration, but with an enhancement at low concentration and (ii) absence of EPR signals of Gd^{3+} and Cu^{2+} in the superconducting specimens. These two aspects are addressed to in this paper.

2. Dependence of T_c on concentration of Gd/y

The value of transition temperature T_c has been found to be dependent on the Gd^{3+}/Y^{3+} concentration. The fact that a similar behaviour was observed both with paramagnetic ion, Gd^{3+}, and diamagnetic Y^{3+} ion suggests that it is not associated with spin scattering processes. Further, it was observed that T_c indeed goes up by about 15 K for a concentration of $x = 0{\cdot}25$, beyond which T_c went down drastically and superconductivity could not be detected down to 20 K for $x = 0{\cdot}5$. This behaviour is in marked contrast to a number of reports suggesting monotonic decrease of T_c with increase of x. Our findings were confirmed recently by Clayhold *et al* (1989) who reported a similar non-monotonic variation of T_c with x in Tm-doped $Bi_2Sr_3Ca_3Cu_4O_8$ which they attributed to non-monotonic variation of Hall mobility. In view of the similarity in behaviour of T_c with x (i.e. non-monotonous variation) it is quite probable that similar mechanism may be operative in all these compounds. One way of understanding this can be by proposing the possible existence of strains (Clayhold *et al* 1988) in undoped Bi-compound, hindering the movement of carriers which somehow get relieved under the influence of rare-earth substitution. Another mechanism which appears to us as more probable is as follows: At low concentration of $(Gd/Y)^{3+}$ these ions enter the lattice of Ca-site, as expected, changing the mixed valence ratio Cu^{2+}/Cu^{3+} in Cu–O planes. This might in turn help in the stability of superconducting phases at slightly higher temperatures. However, with further increase of Gd/Y^{3+} concentration, the changes in oxygen content may influence T_c; possible occupancy of Gd/Y ions on Cu–O planes also cannot be ruled out.

3. Absence of EPR signals

In the superconducting samples ($x < 0{\cdot}5$), no EPR signals either due to Gd^{3+} or Cu^{2+} were observed in our investigations. We have observed weak signals due to Gd^{3+} only in nonsuperconducting samples ($x = 0{\cdot}5$) at low temperature. Whereas EPR of Gd^{3+} was reported in $YBa_2Cu_3O_{7-x}$, no EPR signals of Cu^{2+} were observed in any of the high T_c superconductors. Shalteil *et al* (1989) clearly showed that Gd^{3+} probe experiences spin-fluctuations at Cu-sites and this results in exchange narrowing of 7-fine structure lines of Gd^{3+} in certain orientations of the crystal. This work supported the NMR results suggesting magnetic spin fluctuations on copper (Pennington *et al* 1989). The non-observation of Cu^{2+} EPR signals from pure phases is rather puzzling and this curious case of the absence of EPR of Cu^{2+} has been very effectively highlighted by Mehran and Anderson (1989). The possibility that the absence of EPR is due to fast spin-lattice relaxation times ($< 10^{-10}$ s) in the metallic state has not been considered most probable as the "EPR silence" of Cu^{2+} was also reported in the antiferromagnetic insulating regimes and also in CuO. Mehran and Anderson (1989) argued that the EPR silence (of Cu^{2+}) is either due to anisotropic antiferromagnetic fluctuations with significantly large correlation lengths or due to some other reason which may not be describable with the formalism of localized spin 1/2 (Cu^{2+}) ions coupled by predominantly Heisenberg exchange interactions. EPR studies of Gd^{3+} in $YBa_2Cu_3O_{7-x}$, of Shaltiel *et al* (1989) have shown that the relaxation rate appreciably increased close to, but above T_c and they concluded that EPR results suggest the possibility of spin pairing just above T_c (a somewhat similar mechanism was suggested earlier by Sastry *et al* 1987).

The absence of Gd^{3+} and Cu^{2+} signals in Bi-compounds investigated in our study certainly point towards a fast spin lattice relaxation processes in these materials. One aspect that has not been considered so far is the energy exchange between spin-system and the fluxon-lattice that exists in these superconductors at fields higher than ~ 100 G. It is now clearly established that a strong non-resonant microwave absorption occurs (see, for example, Maniwa *et al* 1988; Pakulis and Chandrashekhar 1988b; Pakulis and Osada 1988a), which increases with increase of magnetic field. This absorption is attributed to 'fluxon-flow'. Therefore at magnetic fields greater than few tens of Gauss, the "lattice" in superconducting materials consists of an additional pathway of energy exchange which is non-resonant and very effective. In our opinion, in addition to all other mechanisms this should be quite a dominant process, more so if these impurities act as flux-pinning centres.

References

Baberschkie K 1976 *Z. Phys.* **B24** 53

Clayhold J *et al* 1988 *Phys. Rev.* **B38** 7016

Clayhold J, Hagen S J, Ong N P, Tarascon J H and Barboux P 1989 *Phys. Rev.* **B39** 7320

Maniwa Y, Grapp A, Hentsch A and Mehring M 1988 *Physica* **C156** 755

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

Pakulis E J and Osada T 1988a *Phys. Rev.* **B37** 5940

Pakulis E J and Chandrasekhar G V 1988b *Phys. Rev.* **B38** 11974

Pennington *et al* 1989 *Phys. Rev.* **B39** 2902

Sampathkumaran E V, Sastry M D and Kadam R M 1989 *Physica* **C159** 267

Sastry M D, Dahri A G I, Babu Y, Kadam R M, Yakhmi J V and Iyer R M 1987 *Nature (London)* **36** 8309

Shaltiel D *et al* 1989 *Physica* **C161** 13