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Cooperative effect of Zn and Ga doping in $YBa_2Cu_3O_7$

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Abstract. The creation of local magnetic moments at the plane and chain Cu-sites in $YBa_2Cu_3O_7$ due to incorporation of Ga^{3+} and Zn^{2+} has been studied with respect to the superconducting transition temperature and structural parameters of the compound. The result indicates that the local moments are created due to slowing down of spin and charge fluctuations in the planes and chains respectively due to doping.

Keywords. Doping; spin charge fluctuation; local moments.

1. Introduction

Substitution by metal ions at the Cu site in $YBa_2Cu_3O_{7-y}$ (YBCO)-type superconductors leads to a generally unfavourable effect on superconductivity but in different degrees for different dopant metal ions (Maeno *et al* 1987; Oda *et al* 1987; Xiao *et al* 1987; Hiroi *et al* 1988). Divalent ions viz Zn^{2+} substituting Cu(2) preferentially in the Cu–O_2 planes have been shown to drastically lower the superconducting transition temperature ($dT_c/dx = -14$ K/at.%) while retaining the basic orthorhombic structure of YBCO (Xiao *et al* 1988a; Majumder *et al* 1988). On the other hand preferential substitution of trivalent ions like Al^{3+} and Ga^{3+} for Cu(1) at the Cu–O chain site in very small concentrations induces crystallographic phase transition (orthorhombic to tetragonal) without affecting the superconducting properties significantly (Bridges *et al* 1989; Xiao *et al* 1988b). There is not much change in the superconducting transition temperature (T_c) across the orthorhombic to tetragonal transition.

Though the Cu–O_2 planes are known to play a crucial role regarding superconductivity in all the known cuprate oxide superconductors, the importance of integrity of the chains in determining the superconducting behaviour in YBCO-type superconductors is clearly borne out by the systematic reduction of T_c, accompanied by orthorhombic to tetragonal transition with removal of oxygen from the Cu–O chains (Cava *et al* 1988). Thus, to obtain a deeper insight into the superconductivity in YBCO-type superconductors, the effect of substitution at the plane and chain sites of Cu in contrast with the effect of oxygen stoichiometry on various properties is due. Since Cu is thought to be in two valence states (2+ and 3+) in YBCO, we have attempted to study the combined effect of a 2+ ion (Zn^{2+}) and a 3+ ion (Ga^{3+}) on superconductivity when present together in the lattice.

2. Experimental

Samples of $YBa_2(Cu_{0.95}Zn_{0.05-x}Ga_x)_3O_{7-y}$ ($x = 0, 0.012, 0.025, 0.038, 0.05$) were prepared by solid-state reaction of constituent oxides and $BaCO_3$ in the required proportions. The mixture was calcined at 900°C in air for 12 h and cooled to room temperature over a period of 10 h. This process of heating and grinding was carried out three times in each case. Finally, the samples were pressed into discs and heated in oxygen atmosphere at 950°C for 12 h, 700°C for 2 h and 450°C for 1 h and cooled to room temperature over a period of 10 h. Powder X-ray diffraction patterns were taken using Cu–K_α radiation. The values of the cell parameters were determined using a least square fitting procedure. Resistivities of the samples were measured by the standard four-probe method in the temperature interval 300 K to 4.2 K.

3. Results and discussion

The Zn-doped sample has the orthorhombic distortion (δ) close to that of the undoped YBCO system, whereas the Ga-doped sample shows almost tetragonal structure (figure 1). The structure of YBCO is basically dictated by oxygen ordering (Cava *et al* 1988) and the charge state of Cu(1) ions (Soderholm *et al* 1987) in the Cu–O chains. In agreement with neutron diffraction studies (Majumder *et al* 1988), the above result on structural changes due to incorporation of Zn and Ga indicates that Zn preferentially substitutes for Cu(2) at the plane site where it does not affect either the oxygen vacancy ordering or the charge state of Cu(1) ions and Ga substitute for Cu(1) at the chain site where it can affect both.

Since Ga^{3+} substitutes Cu preferentially at the chain site, the Cu–O_2 planes where the actual superconduction occurs are not directly affected. Therefore, T_c is not affected by Ga^{3+} doping as much as it is affected by doping Zn^{2+} which preferentially substitutes Cu at the plane site (figure 2). However, the Cu–O chains acting like charge reservoir (Cava *et al* 1988) control the carrier density in the Cu–O_2 planes. Incorporation of Ga^{3+} in the chains reduces formal valence of Cu from 3+ to 2+ and thus reduces the carrier (hole) density in the planes. By whatever amount the

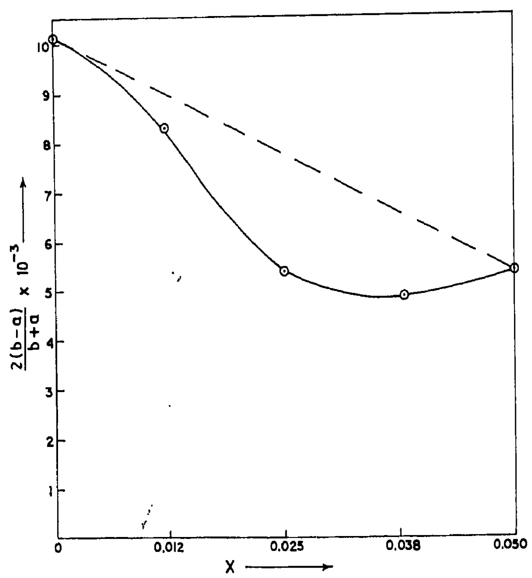

Figure 1. Variation of orthorhombic distortion as a function of Zn–Ga concentration in YBCO.

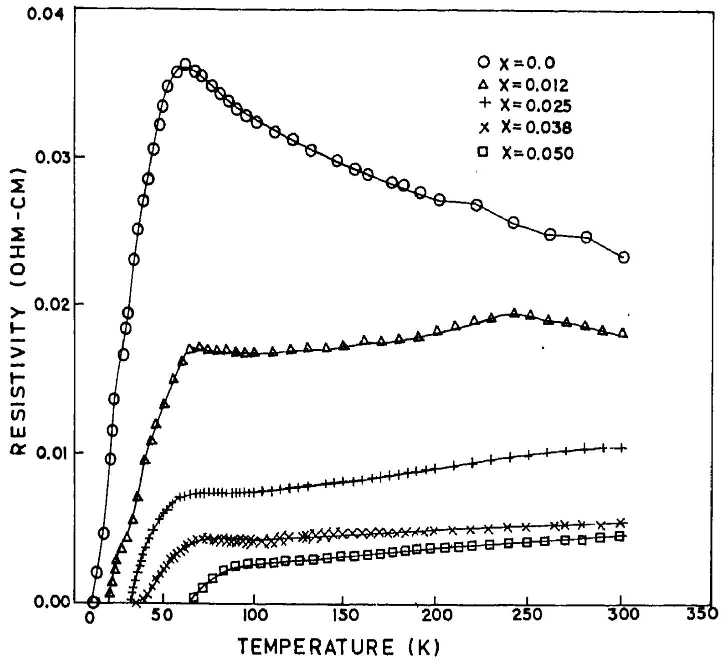

Figure 2. Temperature dependence of resistivity for YBCO compounds with varying Zn and Ga concentration.

T_c is reduced due to Ga^{3+} doping is perhaps due to the indirect effect of reducing the carrier concentration in the planes via charge reduction in the chains.

Incorporation of Zn^{2+} in Cu–O_2 planes has a dramatic effect on superconducting transition temperature (figure 2). Zn^{2+} is a nonmagnetic and stable 2+ ion. The presence of such ions disturbs the antiferromagnetically-coupled spin fluctuations in the Cu–O_2 planes leading to formation of local moments (Ponte *et al* 1988; Jee *et al* 1988). According to many theories (Mathur *et al* 1988; Aharony *et al* 1988; Hirsch *et al* 1988) the antiferromagnetically-coupled spin fluctuations are essential for superconductivity in the cuprate systems. The local moments developed due to slowing down of such fluctuations in Zn-doped YBCO samples reduce the strength of Cooper pairs. Hence T_c is reduced drastically due to Zn doping. However, the carrier density being intimately linked with the charge state of Cu is not much affected by doping with Zn^{2+}. To explain the semiconducting behaviour of resistivity arising due to Zn^{2+} substitution while Zn^{2+} is not affecting the carrier concentration, we must consider the band structure calculation in YBCO compounds (Mattheiss 1987). The $d_{x^2-x^2}$ band of Cu^{2+} in oxide superconductors is usually broad (10 eV compared to 1 eV in NiO). The band gap as determined from optical experiments (Ginder *et al* 1988) is relatively large (2 eV), indicating a localized behaviour. However, comparing the band gap to the overall unrenormalized bandwidth (10 eV), one arrives at the opposite conclusion. The presence of Zn^{2+} in the Cu–O_2 is expected to reduce the overall bandwidth and hence induce localization. This would lead to the semiconducting type of temperature dependence of normal state resistivity as observed in figure 2.

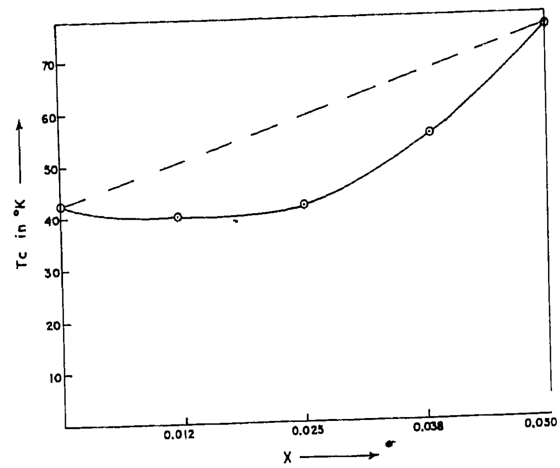

Figure 3. Variation of the mid-point of superconducting transition (T_c) as a function of Zn–Ga concentration in YBCO.

The enhanced reduction of T_c (figure 3) and orthorhombic distortion (figure 1) when Ga-ions and Zn-ions are present together, we believe, suggest an interplay between the local magnetic moments which appear as a consequence of the doping of the lattice at both the sites. It is reasonable to assume that Ga doping leads to moment formation only in the chains and that these moments directly do not influence superconducting behaviour of the planes if the integrity of the planes is not disturbed. But once there are moments in the planes as well (due to Zn doping) a coupling of these moments to the Ga-induced moments in the chains causes further localization and bring down T_c and orthorhombic distortion further.

4. Conclusion

In conclusion our study has revealed the following aspects of the effect of substitution at the Cu sites by Zn and Ga on the superconducting and normal state properties of YBCO type systems. Zn^{2+} and Ga^{3+} preferentially substitute for Cu at the plane and the chain sites respectively which is in agreement with Xiao *et al* (1988a) and Majumder *et al* (1988) and contradicts the conclusion of Kajitani *et al* (1988). The presence of Zn^{2+} in the Cu–O_2 planes breaks the coupling between Cooper pairs and hence drastically affects superconductivity in YBCO-type systems. Ga^{3+} on the other hand indirectly affects the superconductivity by decreasing the carrier concentration in Cu–O_2 planes through reduction of charge state of Cu from 3+ to 2+ in Cu–O chains. The carrier density in Cu–O_2 planes is not affected by Zn^{2+} doping. Yet the semiconducting type of temperature dependence of resistivity as observed in Zn-doped samples can still be explained if the $d_{x^2-y^2}$ band narrows down due to the incorporation of Zn. The local moments are formed due to slowing down of spin fluctuations in the planes and slowing down of charge fluctuations in the chains because of the presence of Zn and Ga.

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