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Effect of oxygen deficiency (δ) on transition temperature of yttrium cuprate superconductors

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Abstract. The nature of pairing mechanism as well as transition temperature of yttrium cuprates is discussed using the strong coupling theory. An interaction potential has been developed for the layered structure with two conducting CuO_2(a-b) layers in a unit cell. The interaction potential properly takes care of electron–electron, electron–phonon and electron–plasmon interactions. Furthermore, the electron–phonon coupling parameter (λ), the modified Coulomb repulsive parameter (μ^*) and the 2D acoustic phonon (plasmon) energy as a function of oxygen deficiency is worked out. Finally, the superconducting transition temperature (T_c) is then evaluated by using these coupling parameters and obtained $T_c = 95(92)$K for $Y(Yb)Ba_2Cu_3O_{7-\delta}$ superconductors with $\delta = 0{\cdot}0$. The model parameters estimated from the layered structure approach are consistent with the strong coupling theory. The result deduced on the variation of T_c with δ are in fair agreement with the earlier reported data on yttrium cuprates. The analysis of the above results are discussed.

Keywords. Oxygen deficiency; phonons; plasmons; coupling parameter; superconducting transition temperature.

1. Introduction

The discovery of superconductivity in the layered copper oxides with lanthanum as rare-earth ($T_c \cong 40$K) has stimulated an extensive theoretical and experimental work (Bednorz and Muller 1986). Subsequently, the announcement of $YBa_2Cu_3O_{7-\delta}$ as a superconductor with $T_c = 90$K (Wu *et al* 1987) has renewed the interest. Both the cuprates have in general a common feature of conducting CuO_2 planes. The copper charge valence neutralities is perturbed either by doping concentration (x) (e.g. in $La_{2-x}Sr_xCuO_4$) or by oxygen deficiency (δ) (as in $YBa_2Cu_3O_{7-\delta}$). The layered structure consists of strong superconducting planes and the transport is mostly conveyed along the strongly superconducting CuO_2 (a-b) planes. It is believed that the crystal structure and transport properties of YBCO are strongly dependent on the oxygen deficiency (δ). It may be noted that for the lower values of δ ($= 0{\cdot}0$) the phase is orthorhombic and becomes superconducting at low temperatures. Furthermore, for higher values of δ ($= 1{\cdot}0$), the phase is tetragonal and non-superconducting at all temperatures. In fact the behaviour of transition temperature (T_c) with oxygen deficiency is anomalous and has been noticed since their discovery. It is therefore necessary to understand the behaviour of T_c with δ from the point of view of theory.

The yttrium cuprates contain two-dimensional (2D) conducting CuO_2 planes as well as one-dimensional (1D) CuO chains. The role of chains in the conduction mechanism is not yet clearly understood. Cava *et al* (1990) and Kerkels *et al* (1992) have reported the behaviour of transition temperature with oxygen deficiency (δ) in $YBa_2Cu_3O_{7-\delta}$

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superconductors. It is observed that T_c varies smoothly showing two plateaus with δ in the range $0{\cdot}0 < \delta < 1{\cdot}0$. Furthermore, the T_c varies stepwise from near 90K [$0{\cdot}0 < \delta < 0{\cdot}2$] and decreases rapidly to about 60K [$0{\cdot}2 < \delta < 0{\cdot}3$]. It is nearly constant in the range $0{\cdot}3 < \delta < 0{\cdot}5$ and then drops sharply from 60K to 0K for $0{\cdot}5 < \delta < 0{\cdot}6$. The first plateau is observed at about 90K for an oxygen content 0·0 to 0·2 and a second plateau is present at 60K over the oxygen deficiency smaller than 0·6. It is understood that in yttrium cuprates, the superconductivity is sensitive to oxygen deficiency (δ). Kerkels *et al* (1992) have extensively studied the effect of substitution of Y ion by Sm and Yb ions in these cuprates. Similar results on the behaviour of T_c with δ have been observed as those of Y doped superconductors with a negligible change in maximum superconducting T_c at $\delta = 0{\cdot}0$.

With regard to pairing mechanism it may be noted that it is extremely difficult to achieve a transition temperature of 40K or more based on the conventional electron–phonon interactions. Over the last several years the plasmon mechanism emerged in the central theme which is not only important in the additional pairing but could also lead to such high T_c values. Earlier Jha (1987) emphasized the role of plasmons in YBCO superconductors and explained the high T_c. Later on, Tewari and Gumber (1990) predicted the high T_c and the anisotropic properties in the layered structure YBCO systems. They pointed out that the plasmons were able to form an additional pairing mechanism in yttrium copper oxide superconductors. Earlier, Singh *et al* (1993) investigated the effects of two dimensional (2D) acoustic plasmons and succeeded in predicting the composition dependence of the transition temperature in $La_{2-x}(Ba, Sr)_xCuO_4$ superconductors. Besides these theoretical predictions, the plasmons were observed by electron–energy loss spectroscopy in $YBa_2Cu_3O_{7-\delta}$ superconductors (Bozovic 1990). Recently Varshney and Singh (1995) devoted their effort to develop a mechanism (joint phonon–plasmon) based on free electron layered electron gas (FELEG) model of quasi two dimensional layers in lanthanum cuprates with single CuO_2 layer. The approach facilitates the dielectric function and dispersion relations of phonon and plasmon modes. It was noticed that joint phonon–plasmon mechanism with properly incorporated layered structure in the interaction potential not only described the pairing mechanism but also explained consistently the superconducting state parameters too. Motivated from the experimental observations (Cava *et al* 1990; Kerkels *et al* 1992) and earlier theoretical investigations (Jha 1987; Tewari and Gumber 1990; Singh *et al* 1993; Varshney and Singh 1995), we thought it pertinent to look for the pairing mechanism and behaviour of transition temperature with oxygen deficiency (δ) in yttrium cuprates. In the present study, we have extended the earlier approach (Singh *et al* 1993; Varshney and Singh 1995) by considering two conducting (2D) CuO_2 planes in a unit cell. The main feature of the developed approach is to estimate the electron–phonon coupling parameter (λ), the modified Coulomb repulsive parameter (μ^*) and the 2D acoustic phonon (plasmon) $\hbar\omega_-$ ($\hbar\omega_+$) energy to evaluate the superconducting transition temperature in yttrium cuprate as a function of oxygen deficiency. We have made an effort to understand the experimental observations on T_c with δ based on realistic parameters by a simple layered electron gas which properly incorporates the layered structure.

The plan of the present study is as follows. In § 2 we develop the interaction potential by considering two conducting 2D CuO_2 layers in a unit cell separated by insulating layers. We work out the coupling parameters and the energy of the generated polarized waves along the a-b plane. In the present study we have not considered the role of

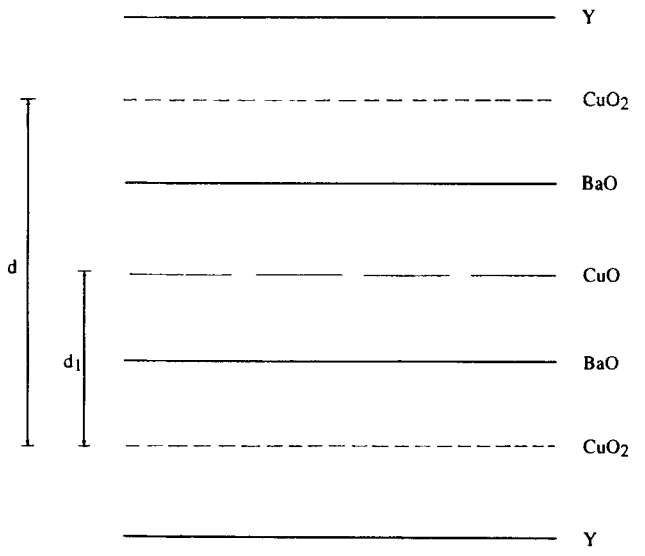

Figure 1. Layered structure of $YBa_2Cu_3O_{7-\delta}$ superconductors.

chains due to the fact that they will act as a reservoir and their effects will be studied separately. From the deduced coupling parameters in the strong coupling theory the transition temperature as a function of oxygen deficiency is estimated. The results obtained from the simple approach are analysed and discussed in § 3. Finally, § 4 is devoted to conclusions.

2. Theoretical formalism

The change in oxygen deficiency (δ) in $ABa_2Cu_3O_{7-\delta}$ (A = Y, Yb) superconductors is believed to introduce free charge carriers (holes) in the conducting CuO_2 planes. These charge carriers interact by way of Coulomb potential with the nearby CuO_2 planes. Consider a set of two dimensional (2D) layered electron gas where the charge carriers interact by polarized waves (quantized lattice vibrations and collective excitations). The layered structure of $YBa_2Cu_3O_{7-\delta}$ is regarded as the stack of planes Y, CuO_2, BaO, oxygen deficient CuO (chain), CuO_2, BaO, CuO_2, Y (see figure 1). It is assumed that a unit cell consists of 2D layers in the a-b plane with a relatively weak coupling between the planes in the z-direction. We made following assumptions: (i) there are two conducting CuO_2 planes per unit cell, (ii) the CuO_2 planes form an infinite array of planes along c-axis, (iii) the non-conducting planes between CuO_2 planes are considered as an uniform dielectric medium with a background dielectric constant (ε_0) and (iv) the oxygen deficient CuO chain stabilized the charge carriers in the conducting plane.

The effective interaction potential between charge carriers is expressed as

$$V(q,\omega) = \frac{V_c(q)}{\varepsilon(q,\omega)}, \tag{1}$$

with $V_c(q)$ is the bare Coulomb potential, $\varepsilon(q,\omega)$ the longitudinal dielectric function for a single band of charge carriers and q the wave vector along a-b plane.

The Fourier transformed effective potential between the charge carriers is

$$V(q, q_z, \omega) = \frac{2\pi e^2}{q\varepsilon_0} \frac{S(q, q_z)}{\varepsilon(q, q_z, \omega)}. \tag{2}$$

Here, $S(q, q_z)$ is the structure factor as

$$S(q, q_z) = \frac{\sin h(qd)}{\cos h(qd) - \cos(q_z d)}, \tag{3}$$

with d as the distance between the two CuO_2 planes in a unit cell, q_z the wave vector in the perpendicular direction and ε_0 denotes the background dielectric constant of the surrounding materials. The longitudinal dielectric response function $\varepsilon(q, q_z, \omega)$ for two CuO_2 planes in a unit cell is

$$\varepsilon(q, q_z, \omega) = 1 + 2P(q, \omega)S(q, q_z) + P^2(q, \omega)S(q, q_z)S'(q), \tag{4}$$

with,

$$S'(q) = \frac{\cos h(qd) - \cos h(qd')}{\sin h(qd)}, \tag{5}$$

and $d' = 2d_1 - d$ with $d_1 = d/3$.

The layered structure superconductors possess anisotropic physical properties and as a matter of fact, it is customary to restrict ourselves to the a-b conduction plane and for this purpose we average (2) over q_z as

$$V(q, \omega) = \frac{d}{2\pi} \int_{-\pi/d}^{+\pi/d} V(q, q_z, \omega) \mathrm{d}q_z. \tag{6}$$

The integral can thus be evaluated using (2)–(6) to get

$$V(q, \omega) = \frac{4\pi e^2 [1 + P(q, \omega)S'(q) + R(q, \omega)] \sin h(qd)}{q\varepsilon_0 [|D^2(q, \omega) - 1|]^{1/2}}. \tag{7}$$

Here

$$R(q, \omega) = \frac{\sin h[q(d - d_1)] + D(q, \omega) \sin h(qd_1)}{\sin h(qd)}, \tag{8}$$

with,

$$D(q, \omega) = \cos h(qd) + 2P(q, \omega) \sin h(qd) + P^2(q, \omega) \sin h(qd) S'(q). \tag{9}$$

The polarization function $P(q, \omega)$ is due to the charge carriers (c) and ions (i)

$$\begin{aligned} P(q, \omega) &= P_c(q, \omega) + P_i(q, \omega) \\ &= \frac{2\pi e^2 n_c q}{m^* \varepsilon_0 [(q^2 V_F^2)/2 - \omega^2]} - \frac{2\pi e^2 n_i Z^2 q}{M \varepsilon_0 \omega^2}, \end{aligned} \tag{10}$$

where $n_c(n_i)$ denotes the 2D charge carriers (ionic) density, Ze the sum of ionic and bound electronic charge, V_F the Fermi velocity, m^* the effective mass of the charge carriers and M the mass of unit cell, respectively.

The interaction potential $V(q, \omega)$ properly incorporates the effect of electron–electron, electron–phonon and electron–plasmon interactions as well as the structure

factor. The interaction energy is attractive if

$$D(q,\omega) < 0, \tag{11}$$

and is responsible for pairing mechanism. In the long wavelength limit ($q \to 0$), the interaction potential leads to

$$V(q,\omega) = \frac{4\pi e^2 d}{\varepsilon_0}\varepsilon^{-1}(q,\omega),$$

with,

$$\varepsilon^{-1}(q,\omega) = \frac{1 + P(q,\omega)S'(q) + R(q,\omega)}{[|D^2(q,\omega) - 1|]^{1/2}}. \tag{12}$$

Zero's of the dielectric function will yield the frequencies of coupled 2D acoustic plasmon and phonon modes. In the long wavelength limit, the frequencies are deduced as

$$\omega_+^2 = \$^2 + \alpha\omega_{\mathrm{Pi}}^2, \tag{13}$$

$$\omega_-^2 = \alpha\omega_{\mathrm{Pi}}^2[1 + \alpha\omega_{\mathrm{Pi}}^2/\$^2]^{-1}. \tag{14}$$

Here, $\omega_{\mathrm{Pi}}(\omega_{\mathrm{Pi}})$ are the usual 2D electron (ion) plasmon frequency, $\alpha = qd$ and $\$^2 = q^2 V_{\mathrm{F}}^2/2$.

In order to calculate the superconducting transition temperature one requires the knowledge of modified Coulomb repulsive parameter (μ^*) and the coupling parameter (λ) between neighbouring electrons. For this, the real and imaginary parts of the interaction potential is evaluated from (12) as

$$\text{Real } V(q,\omega) = \frac{4\pi e^2}{q\varepsilon_0}\frac{\omega^2}{(\omega^2 - Cq)}, \tag{15}$$

and

$$\text{Imaginary } V(q,\omega) = \frac{4\pi e^2}{q\varepsilon_0}\pi C q\,\delta(\omega^2 - Cq). \tag{16}$$

Here, $\delta(\omega^2 - Cq)$ is the Dirac delta function and $C = \omega_{\mathrm{Pi}}^2/q\varepsilon_0$. The Coulomb repulsive parameter (μ) is expressed as

$$\mu = \frac{N(0)}{2K_{\mathrm{F}}^2}\int_0^{2K_{\mathrm{F}}} \text{Real } V(q,\omega)q\,\mathrm{d}q$$

$$= \frac{2\pi e^2 \mathrm{d}}{\varepsilon_0}N(0)\mathrm{Ln}\left[\frac{2+K}{K}\right], \tag{17}$$

with $K = 2d/a_{\mathrm{B}}$, $N(0)$ as the density of states per unit cell and a_{B} is the Bohr radius.

Finally, the modified Coulomb repulsive parameter (μ^*) representing the electron–electron interaction for the maximum value of phonon frequency is

$$\mu^* = \frac{\mu}{1 + \mu\mathrm{Ln}(E_{\mathrm{F}}/\hbar\omega_-)}, \tag{18}$$

with E_{F} as the Fermi energy and $\hbar\omega_-$ denotes the 2D acoustic phonon energy.

The electron–phonon coupling parameter (λ) is derived from the Eliashberg function $\alpha^2(\omega)F(\omega)$ through (Eliashberg 1960)

$$\lambda = 2\int_0^{\omega_-} \frac{\alpha^2(\omega)F(\omega)}{\omega}\mathrm{d}\omega, \tag{19}$$

with $F(\omega)$ as the phonon density of state and $\alpha^2(\omega)$ as coupling strength between electrons and phonons. The coupling parameter is deduced from the Imag. $V(q,\omega)$ as

$$\alpha^2(\omega)F(\omega) = \frac{N(0)}{2K_F^2}\int_0^{2K_F} \text{Imag. } V(q,\omega)q\mathrm{d}q$$

$$= \frac{N(0)\pi^2 e^2\omega^2 \mathrm{d}}{\varepsilon_0 C K_F^2(1-\omega_-)^{1/2}}. \tag{20}$$

Thus, the electron–phonon coupling parameter is obtained as

$$\lambda = \frac{\omega_-^2}{2a_B K_F^2 C}. \tag{21}$$

Using the above expression for λ, μ^* and ω_-, the superconducting transition temperature (T_c) due to phonons alone is (Ruvalds 1987)

$$T_c^{Ph} = 0{\cdot}7\omega_- \exp\left[-\frac{1+\lambda}{\lambda-\mu^*}\right]. \tag{22}$$

When one considers the presence of both 2D acoustic phonons and plasmons, the total T_c is (Kresin 1987)

$$T_c = T_c^{Ph}\left[\frac{\hbar\omega_{Pl}}{T_c^{Ph}}\right]^h, \tag{23}$$

where

$$h = \frac{\lambda_{Pl}}{\lambda+\lambda_{Pl}}. \tag{24}$$

λ_{Pl} denotes the electron–plasmon coupling strength.

Using the developed expressions following the strong coupling theory, we have obtained the coupling parameters (λ and μ^*) and 2D acoustic phonon (plasmon) modes as a function of oxygen deficiency to compute the variation of superconducting transition temperature with oxygen deficiency in $ABa_2Cu_3O_{7-\delta}$ superconductors. The analysis is presented and discussed in the following section.

3. Results and discussion

In order to calculate the superconducting transition temperature (T_c) in $ABa_2Cu_3O_{7-\delta}$ (A = Y, Yb) superconductors, we have used the realistic parameters based on the experimental data. The effective mass is evaluated from the electronic specific heat coefficient (γ) value as $1{\cdot}5m_e$ for $YBa_2Cu_3O_{7-\delta}$ superconductors (Inderhees *et al* 1987). For $YbBa_2Cu_3O_{7-\delta}$ system, we used $m^* = 1{\cdot}6m_e$, although no

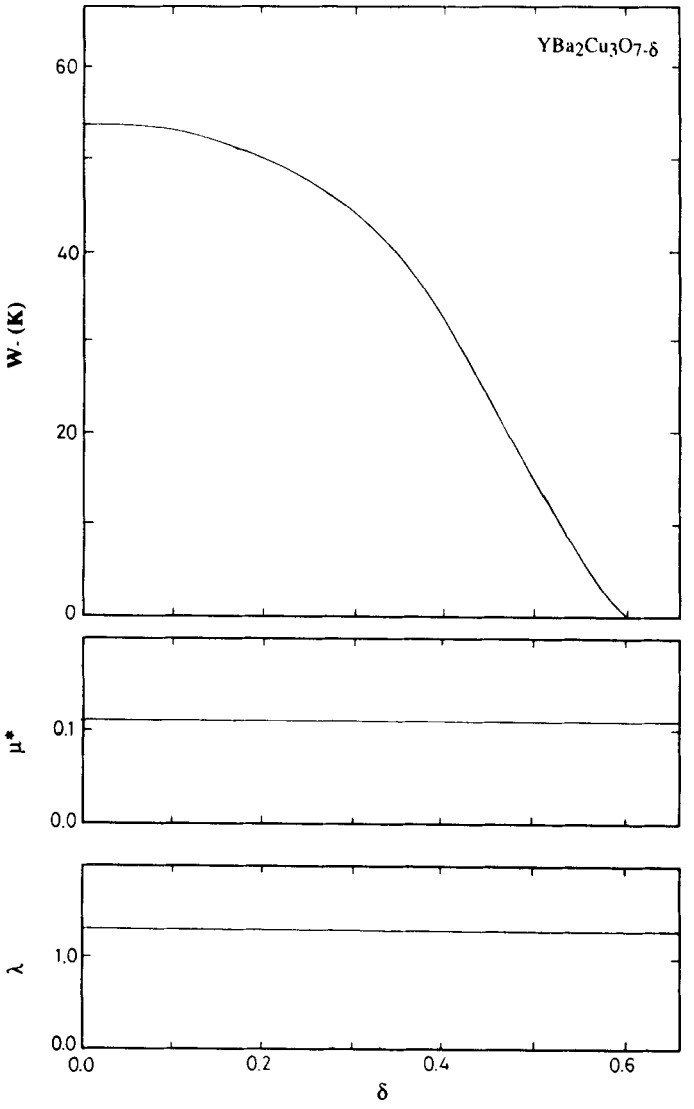

Figure 2. Variation of $\omega_{\_}(K)$, μ^* and λ with δ in $YBa_2Cu_3O_{7-\delta}$ superconductors.

experimental data on electronic specific heat coefficient is available, so we choose it accordingly. The mass of a unit cell is 12·77 amu and the background dielectric constant ε_0 is taken as 4·5 (Bozovic 1990) from the electron energy loss spectroscopy. The charge carrier density and ionic density are evaluated from the lattice parameters. Taking $a = 3{\cdot}8136$ Å, $b = 3{\cdot}8845$ Å and $c = 11{\cdot}6603$ Å (Cava *et al* 1990) we obtained $n_c = 2{\cdot}38 \times 10^{14}\,\mathrm{cm}^{-2}$ and $n_i = 6{\cdot}74 \times 10^{14}\,\mathrm{cm}^{-2}$ at $\delta = 0{\cdot}0$. It is customary to make them oxygen deficient (δ) dependence as

$$n_{c(i)}(\delta) = n_{c(i)}(\delta = 0{\cdot}0)[\exp -(\delta/\delta_c)^2]. \tag{25}$$

We choose $\delta_c = 0{\cdot}4$. The sum of ionic and bound electronic charge $Ze = -2e$.

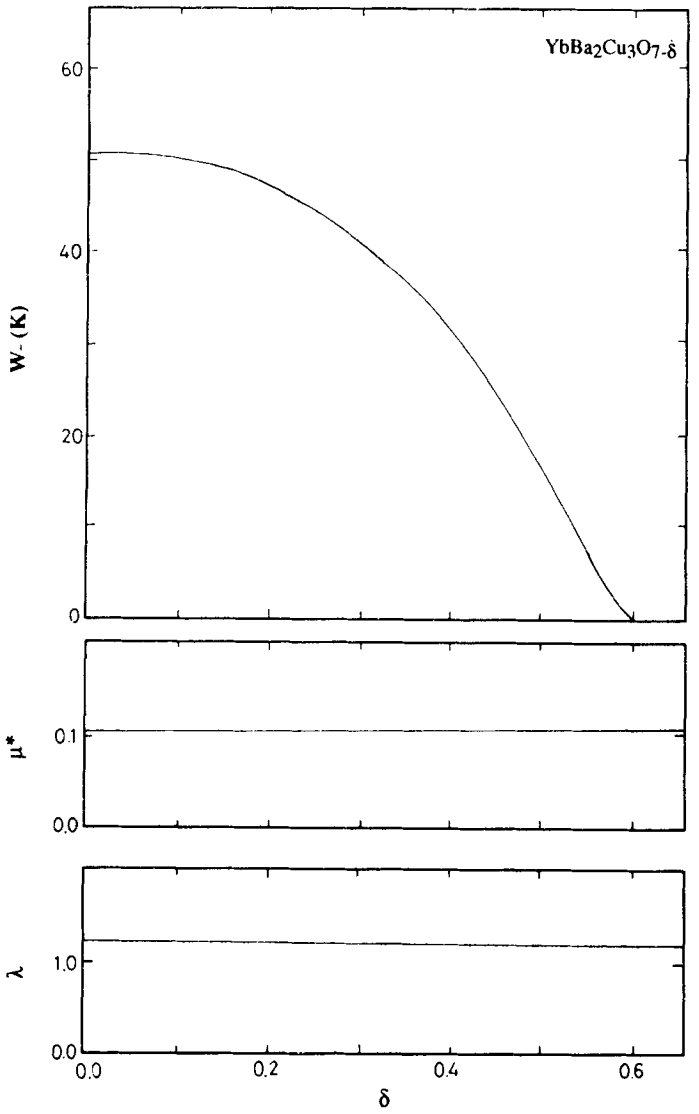

Figure 3. Variation of $\omega_{-}(K)$, μ^* and λ with δ in $YbBa_2Cu_3O_{7-\delta}$ superconductors.

The coupling parameters (λ and μ^*) and the 2D acoustic phonon energy ($\hbar\omega_{-}$) as discussed in previous section have been plotted as a function of δ in figures 2 and 3 for $YBa_2Cu_3O_{7-\delta}$ and $YbBa_2Cu_3O_{7-\delta}$ superconductors, respectively. The electron–phonon coupling parameter (λ) is deduced as 1·28 (1·20) for Y (Yb), respectively. It is seen from the figures that λ remains almost constant for the whole oxygen deficiency range. The estimated value of $\lambda > 1{\cdot}0$ favours the strong coupling theory. The screened Coulomb repulsive parameter μ^* is obtained as 0·11 (0·10) for Y (Yb) cuprate superconductors and its behaviour with δ is almost constant. The 2D acoustic phonon energy is obtained as 46 (42) meV for Y (Yb). This is in accordance with the previous Raman measurements (Thomsen and Cardona 1989). It is clear from the figure that

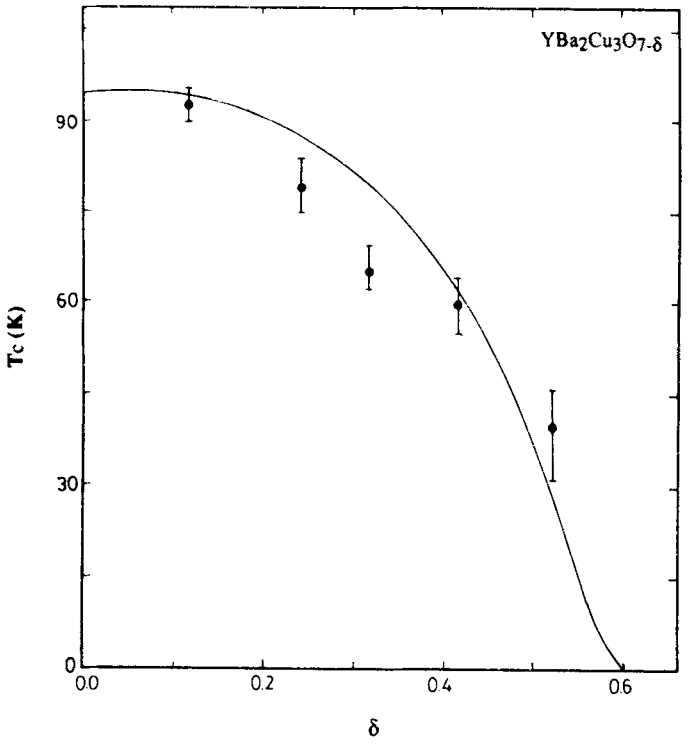

Figure 4. Variation of T_c with δ in $YBa_2Cu_3O_{7-\delta}$ superconductors. Experimental data (♦) are taken from Kerkels *et al* (1992).

ω_- decreases with the increased value of δ. We believed that for the higher values of oxygen deficiency, charge carriers participating in the pairing mechanism is reduced and hence the low density of states. If we consider only phonon mechanism the transition temperature estimated from (22) comes out to be 53·21 (57·00)K for Y (Yb) doped superconductors. The T_c obtained by us with the phonon mechanism is quite low as compared to the experimental data. This motivated us to incorporate the 2D acoustic plasmons. Taking $\lambda_{PI} = 0{\cdot}1$ and $\hbar\omega_+$ as 3 eV from (13), we find that T_c enhances to 95K which is consistent with the reported value of $T_c = 90$K. Hence, there is an enhancement of 78% on T_c values as obtained from the phonon mechanism. For the $YbBa_2Cu_3O_{7-\delta}$ superconductors, we obtained 92K which is in fair agreement with the reported value of $T_c = 89$K.

We have made efforts to understand the behaviour of T_c with δ in $Y(Yb)Ba_2Cu_3O_{7-\delta}$ superconductors and is shown in figures 4 and 5. From the proposed theory with 2D conducting CuO_2 layers in a unit cell we obtained the variation of T_c with δ similar to those reported earlier. It is found that with the increase of δ the T_c drops linearly and is zero for $\delta = 0{\cdot}6$. Furthermore, the theory fails to predict the second plateau which occurs in the range $0{\cdot}3 < \delta < 0{\cdot}5$. We believe that the second plateau might be due to the phase transition occurring in this region. The deduced results are consistent with the reported reports and is attributed to the proper care of layered structure with two conducting CuO_2 planes in a unit cell of yttrium cuprates.

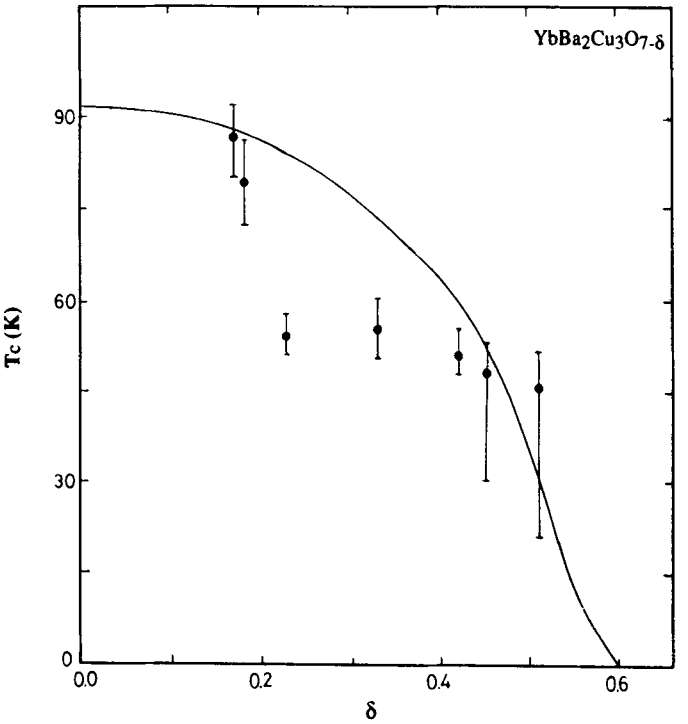

Figure 5. Variation of T_c with δ in $YbBa_2Cu_3O_{7-\delta}$ superconductors. Experimental data (♦) are taken from Kerkels *et al* (1992).

4. Conclusions

In the present investigation, we have systematically investigated the pairing mechanism in yttrium cuprates by considering two conducting CuO_2 planes in a unit cell. The model potential properly incorporates the electron–electron, electron–phonon and electron–plasmon interactions. Deduced value of 2D acoustic phonon and plasmon modes are consistent with the Raman measurements and electron energy loss spectroscopy in yttrium cuprates. The coupling parameters as λ and μ^* from the above approach favours the strong coupling theory. It is noticed that the role of 2D acoustic plasmons is to provide an additional pairing mechanism that could lead to such high T_c values. We are able to understand the first plateau observed in the variation of T_c with δ. The obtained variation is quite consistent with the experimental data. Regarding the second plateau observed at T_c of 60 K we feel that this is due to the phase transition and will be studied separately in future. In conclusion, the 2D acoustic phonons together with 2D acoustic plasmons can explain fairly well the pairing mechanism and the superconducting transition temperature in yttrium cuprate superconductors.

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