CHAPTER VI
Suppression of $T_c$ in the ErBa$_2$Cu$_4$O$_8$
system by Pr and Ce dopants
VI.1 Introduction

Bulk superconductivity with $T_c$ around 80K, was observed in YBa$_2$Cu$_4$O$_8$ (known as 124) prepared under high oxygen pressure [1-5]. The 124 phase was reported to possess excellent thermal stability [1] due to its fixed oxygen stoichiometry. This behaviour contrasts to that observed in YBa$_2$Cu$_3$O$_{7-\delta}$, which readily loses oxygen at temperatures above 300°C. The 124 phase can also be prepared at ambient pressure by the use of reaction-rate enhancing compounds [6-7]. Some of the characteristic features of the 124 phase are

1. Oxygen stability and lack of twinning: The tremendous increase of the oxygen stability in the 124 phase takes place due to the increase of the coordination number of oxygen with copper. The increase of the oxygen stability is very important for applications and makes 124 a stoichiometric compound with a very small nonstoichiometric range. Due to the oxygen stability of the double chains, no structural phase transition takes place in the 124 phase up to the decomposition temperature (850°C). Without a phase transition no twinning appears. The double chain fixes the b-axis.

2. Strong dependence of $T_c$ on the hydrostatic pressure: The most interesting property induced by the double chains is the unexpectedly high value of $dT_c/dP = 0.57K/kbar$ [8]. It was assumed that similar to the variation of nonstoichiometry in oxygen deficient 123, where an increase of the oxygen occupancy of the chains leads to contraction of the Cu(2)-O(1) distance and an increase of $T_c$ [9], in 124 hydrostatic pressure leads also to a contraction of the Cu(1)-O(2) distance and an increase of $T_c$. In other words, oxygen deficiency has an analogous result to lattice compression. Neutron diffraction under hydrostatic pressure of 10 kbar showed exactly the expected effect [10], the apical oxygen shifting from the chains to the planes. The increase of transition temperature associated with the contraction of the apical oxygen bond is due to charge transfer from the chains to the planes which leads to a pairing mechanism of the holes in the Cu(2) planes.

3. Anomalous thermal expansion: The investigation of the temperature dependence of the bond lengths in the 124 phase [10] showed, in
contrast to the 123 phase, strong effects near $T_c$. At temperatures lower than 100K, the double chains stiffen and cannot contract further. Therefore, in the superconducting state of 124, the b-axis is essentially fixed.

4. Anomalous compressibility: Recent X-ray high pressure work allowed the measurement of compressibilities and bulk modulus of the 124 phase [11]. The linear compressibilities along the three main crystallographic axes are strongly anisotropic, making the 124 an exception among the high-$T_c$ materials measured so far. Similar to the thermal expansion, the b-axis, which contains the double chains, shows an anomalously small compressibility ($1.0 \times 10^{-3}$ GPa$^{-1}$). The a-axis compressibility is 2.8 times larger and the c-axis 4.5 times larger. The bulk modulus at 301K is, with 112GPa, quite low as compared to 123 with approximately 150GPa [12] and increases at 30K to 122GPa.

5. Variations of $T_c$: Due to the stability of the oxygen in the double chains, the 124 phase is nearly stoichiometric, therefore, variations of $T_c$ due to non-stoichiometry have not been observed. Doping with Ca, however, increases the transition temperature of the 124 phase to 90K [13], contrary to its effect in the 123 phase where $T_c$ decreases. The mechanism of this effect is not yet clear. It has been suggested that calcium substitutes yttrium. The corresponding shift in charges is however not detectable with NQR. Substitution of barium would also be possible, however, the influence on $T_c$ should then come from internal (chemical) pressure due to the much larger ionic radius of Ba. One would expect that such effects should be detected by appreciable contraction of the lattice constants, which is not the case. The original assumption that the increase of $T_c$ is associated with a contraction of the Cu(1)-O(2) bond was confirmed with neutron diffraction: a small decrease was detected.

It is therefore seen that the interesting properties introduced by the double chains in the 124 phase make these compounds model substances for the study of the importance of chains in high-temperature superconductivity. The 124 phase comprises the first set of isostructural, stoichiometric (i.e., with well constrained oxygen content) superconductors, and thus they...
VI.2 Ion size effect of $T_c$ in R-124 system

The substitution of Y by trivalent rare-earth elements in orthorhombic YBa$_2$Cu$_3$O$_{7-\delta}$, with the exception of Ce, Pr, Pm and Tb, yield a superconducting phase with a $T_c$ almost identical to that for the YBa$_2$Cu$_3$O$_{7-\delta}$ compound [14]. It shows that the magnetic moments of the lanthanide ions have a weak effect on the CuO$_2$ sheets (only \(\sim 2\text{Å}^2\) away) [15]. In a conventional superconductor, exchange scattering of conduction electrons by the magnetic moments and the resulting breaking of Cooper pairs causes a rapid suppression of superconductivity. The insensitivity of the superconducting properties to substitution of most of the rare earths for Y is presumably due to their layered structure and the nearly complete lack of interaction between rare-earth and Cu-O sublattices [16]. Experimental values of $T_c$ for the RBa$_2$Cu$_3$O$_{7-\delta}$ samples show that magnetic rare earth ions do not have a pair breaking effect on superconductivity.

The similar chemistry of rare earth elements generally enables various mutual replacements in compounds containing these elements. This is also the case in the YBa$_2$Cu$_4$O$_8$ phase, in which yttrium may be substituted by most of the other rare earth elements from La to Yb without destroying the structure. The dependence of $T_c$ on the lattice parameters is different in the 123 and 124 phases. The critical temperature is slightly increased with increasing volume of the 123 unit cell [17,18] while in the 124 structure an opposite behaviour has been observed [19-21].

The 124 compounds have critical temperatures ranging from 57 to 81 K and vary with structural parameters. In the R-124 compounds containing larger (lighter) rare earth ions, as a- and b-lattice parameters increase $T_c$ and orthorhombic distortion decrease [22]. In contrast, the 123 compounds show $T_c$s increasing with increasing ion size and distortion decreasing [23]. This difference in behaviour of $T_c$ in closely related structures may provide a sensitive test for theoretical models. A unique feature of the 123
compounds is the variable oxygen stoichiometry and reversible oxidation-reduction above 400°C. Varying the oxygen content changes $T_c$ and the normal-state resistivity. An absence of variable oxygen stoichiometry in the 124 phase was conjectured by Marsh et al. [24] on the basis that each oxygen in the two Cu-O layers of the 124 phase is bonded to three Cu ions, in contrast to 123 phase where the oxygen is bonded to only two Cu ions. Structural studies [25] indicate that the oxygen double-chains are fully occupied. The consistent oxygen content should permit precise determination of differences of $T_c$ caused by varying rare-earth magnetic moment as well as ion size.

VI.3 Experimental

The samples of pure, Pr- and Ce- substituted ErBa$_2$Cu$_4$O$_8$ were prepared by the solid state reaction method with Er$_2$O$_3$, Ba(NO$_3$)$_2$, CuO, Pr$_6$O$_{11}$ and CeO$_2$, each of 4N purity as starting materials. These were mixed in the correct stoichiometric ratios required for each sample alongwith 0.2 mole fraction of sodium oxalate (Na$_2$C$_2$O$_4$). The synthesis process is relatively simple involving two steps. In the first step, the homogeneously mixed constituents were prereacted in the powder form for 30 minutes at 900°C and then cold pressed into rectangular bars which were again reacted for 24 hours at 900°C in a continuous flow of oxygen. In the second step the reaction temperature was reduced to 815°C for another 48 hours.

Measurements of the temperature dependence of resistivity of the pure and the substituted Er – 124 samples were carried out using the standard four-probe technique. Air drying silver paste was used to make electrical contacts on the samples. The measurement system was hooked to a HP-216 system controller for automatic data acquisition and processing. The X-ray diffraction patterns of the samples were recorded on a Rigaku D/Max-IIC X-ray diffractometer with CuK$_\alpha$ radiation. L$_{III}$ edges of Er and Pr were also recorded on the Rigaku D/Max-IIC modified for X-ray absorption measurements. The data was recorded on a 2$\theta$ scale in a ± 200eV region from the edge.
VI.4 Results and Discussion

Impurity studies have often provided insight into the mechanisms driving unusual and unexplained phenomena. Substitutions of Co, Ga and Zn for Cu in the high T$_c$ superconductor YBa$_2$Cu$_3$O$_{7-δ}$ have helped to clarify the role played by the unequivalent Cu-sites within the orthorhombic structure [26]. Based on these studies along with others it appears that the pairing of d-holes within the Cu-O planes is responsible for the nearly two-dimensional superconducting properties displayed by YBa$_2$Cu$_3$O$_{7-δ}$.

A very surprising result is that the superconducting properties of RBa$_2$Cu$_3$O$_7$, where R is a rare earth except Ce, Pr and Tb are extremely insensitive to the magnetic character of the R ion [27]. This insensitivity has been attributed to a negligibly small exchange interaction between the conduction electrons in the Cu-O planes adjacent to the R ion and the f-electrons of the R ion. One exception to this behaviour is Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-δ}$ where T$_c$ is depressed [28,29] with increasing x and finally goes to zero.

The substitution of Y by Pr in Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-δ}$ causes decrease in T$_c$ with increase in doping density, while the orthorhombic structure remains unaltered. PrBa$_2$Cu$_3$O$_7$ is isostructural to YBa$_2$Cu$_3$O$_7$, however, it is nonsuperconducting [28] and exhibits metallic behaviour. It has also been shown that Ce doping also depresses T$_c$ with increase of doping density [30].

VI.4.1 Suppression of Superconductivity in PrBa$_2$Cu$_3$O$_7$

Nonsuperconductivity of PrBa$_2$Cu$_3$O$_7$ has been a puzzle ever since the material was made. Several mechanisms have been proposed to explain the suppression of T$_c$ in PrBa$_2$Cu$_3$O$_7$ and Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_7$.

The Pr ion shows either a valence of four, as in praseodymium dioxides, or a valence of three as in PrF$_3$ [31]. Therefore, it was first proposed that the superconductivity is destroyed by the presence of tetravalent Pr ions. When Y is replaced by Pr, some of the electronic holes are neutralized by the extra conduction electrons donated by the tetravalent Pr ions, thereby reducing the electronic hole count believed to be crucial for high T$_c$ superconductivity [32]. The effective magnetic moment of the Pr ion in
$Y_{1-x}Pr_xBa_2Cu_3O_7$ derived from magnetic susceptibility measurements [28] varies between $3.6\mu_B$ for $Pr^{3+}$ and $2.5\mu_B$ for $Pr^{4+}$. This presumably suggested that some $Pr$ ions are tetravalent or the $Pr$ ion in $Y_{1-x}Pr_xBa_2Cu_3O_7$ has a mixed valence [28]. Evidence for the presence of tetravalent $Pr$ ions from electronic transport experiments was also reported [33]. However, several X-ray absorption measurements [34] show that $Pr$ is essentially trivalent in $Y_{1-x}Pr_xBa_2Cu_3O_7$ compounds, thereby disputing the plausible "tetravalency" mechanism for the depression of $T_c$. Therefore, Neukirch et. al. [35] instead speculated that $T_c$ is suppressed through changes in the band structure when $Y$ is substituted by $Pr$ in $RBa_2Cu_3O_7$. That the $Pr$ ion is trivalent in $Y_{1-x}Pr_xBa_2Cu_3O_7$ was also concluded from recent photoelectron spectroscopy measurements [36].

Apart from the "tetravalency" and the band structure change mechanisms already mentioned, a few other mechanisms have also been suggested on the basis of different properties observed between $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_7$ [34, 35]. These include the suggestion that a stronger hybridization between $Pr$ 4f states and conduction bands is responsible for the destruction of the superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_7$ [35]. According to Guo and Temmerman [37], the hybridization between 4f states and conduction bands is much stronger in $PrBa_2Cu_3O_7$, than in other $RBa_2Cu_3O_7$ compounds. Consequently the spin splittings of the important $Cu$-$O$ conduction bands near $E_F$ in the $Pr$ compound are up to ten times larger than, for example, those in the Gd compounds. The calculated sizes of the conduction-band spin splittings in $PrBa_2Cu_3O_7$ are comparable to the Cooper pair binding energy ($2\Delta$). This indicates that the Cooper pairs, or the supercurrent carriers, in the superconducting $YBa_2Cu_3O_7$ are broken up when $Y$ is replaced by $Pr$ and consequently the superconductivity is suppressed. Thus, the magnetic pair-breaking due to the strong coupling between $Pr$ 4f and conduction electrons is suggested as the origin of suppression of superconductivity in $PrBa_2Cu_3O_7$.

However, it still remains unresolved in which way $Pr$ localizes mobile holes in the planes whereby the total concentration of oxygen holes is conserved as $Y$ is substituted by $Pr$ [38]. Newly emerging theories [39] presume that the localization is realized via the hybridized state represented by a linear combination of $Pr^{4+}$ and $Pr^{3+}$ plus ligand hole states whereby the resulting total probability of the 4f (Pr$^{4+}$) configuration is only about 0.15
Sample Name: K24P-10%
Sample Name: Er124Pr40%
Sample Name: Er124Pr60%
Fig. VI.2 R-T plots for the ErPr 124 series
Res. (m-ohms)

Temp. (K)

[d] Pr 40%
Temperature vs. Resistivity Plot

- The x-axis represents Temp. (K), ranging from 0 to 300.
- The y-axis represents Resistivity (m-ohm), ranging from 0 to 70.
- The graph shows an increasing trend with a notable deviation at a specific temperature, indicated by Pr 60%.
VI.4.2 Superconductivity of the Pr doped ErBa$_2$Cu$_4$O$_8$ system

We have seen in the previous section that suppression of superconductivity in the R$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_7$ system has been attributed to two possible mechanisms [40]. The first mechanism involves the filling of mobile holes in the conducting CuO$_2$ planes due to the substitution of Pr ions with a valency greater than +3 and hence implies that the suppression of superconductivity results from a reduced number of carriers in the CuO$_2$ sheets. The second mechanism is pair breaking due to spin-dependent exchange scattering of mobile holes in the CuO$_2$ valence band by Pr ions which have a well-defined magnetic moment. Such a large interaction could be generated by the hybridization of the localized Pr 4f states and adjacent CuO$_2$ valence band states.

While considerable efforts have been made to understand the effect of Pr incorporation in the R-123 system, there are only a few reports [41-43] about the superconducting behaviour of the Pr-substituted R-124 system possessing Cu-O chain networks. It would be worthwhile to study the Pr-doped R-124 system and to examine the possible causes of suppression of superconductivity in them. We have studied the $T_c$ variation as a function of Pr concentration in the ErBa$_2$Cu$_4$O$_8$ system.

Typical X-ray diffraction patterns of the Er-124 samples are shown in Fig. VI.1. The orthorhombicity of the pristine system decreases with increasing Pr content. The values of the lattice constants of the ErPr-124 samples are given in Tab.VI.1. The c-lattice parameter of the various Pr-doped samples was found to change very little with Pr content and is in accordance with reported data [44].

Normalized resistance versus temperature curves of the ErPr-124 series of samples are given in Figs VI.2a-f. In order to achieve a better understanding of the suppression of superconductivity in the R-124 system by the substitution of Pr ions at the rare-earth sites, it would be useful to study other (R$_{1-x}$Pr$_x$)Ba$_2$Cu$_4$O$_8$ systems in order to be sure if we are dealing with universal behaviour. Comparing our results with the results of Agarwal et. al. [45], we find that Pr is more effective in suppressing su-
Fig. VI.3 L_{III} edges of Er in ErPr-124.
Fig. VI.4  \( L_{\text{III}} \) edges of Pr in ErPr–124
Fig. VI. 5 To vs Pr conc. for Y-124, Eu-124 and Er-124 systems
perconductivity in \((\text{Er}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8\) and \((\text{Eu}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8\) than in \((\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8\).

Fig.VI.3 shows the \(L_{\text{III}}\) absorption edges of Er in the \((\text{Er}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8\) system \((x = 0.0 - 0.6)\). The Er edges are characteristic of trivalent Er and we conclude that the Er valence is not affected by the Pr concentration. The \(L_{\text{III}}\) absorption edges of Pr in the 40 at% and 60 at% substituted \(\text{ErBa}_2\text{Cu}_4\text{O}_8\) system are shown in Fig.VI.4. The Pr \(L_{\text{III}}\) edges demonstrate that Pr in the Er-124 system is close to trivalent with an upper limit to the valence of 3.14 for the Pr 40 at% sample and 3.16 for the Pr 60 at% sample. This can be concluded from comparison of the energy position and shape of the absorption edge to those systems in which Pr is known to be in trivalent and tetravalent states. Considering the experimental accuracy of the experimental data as well as the uncertainties in their interpretation, an admixture of Pr\(^{4+}\) of about 10% cannot be excluded. This suggests that the Pr ions are predominantly trivalent and localize, rather than fill, mobile holes in the CuO\(_2\) planes. This leads to the suppression of superconductivity and the metal-insulator transition. The mechanism for localizing the mobile holes would presumably be associated with the Pr 4f and CuO\(_2\) valence band hybridization.

Fig.VI.5 shows a plot of \(T_c\) versus Pr concentration for our system and for the \((\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8\) and \((\text{Eu}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8\) systems taken from reference [18]. The observed results suggest that the variation of \(T_c\) with Pr content, \(x\), in the RBa\(_2\)Cu\(_4\)O\(_8\) system depends not only on the presence of Pr ions but also on the nature of the R ion, which is borne out by the fact that the critical concentration of Pr is different for all three systems. This apart, the data of \(T_c\) versus \(x\) does not fit the predictions of the AG theory [46] which gives a monotonic decrease of \(T_c\) with \(x\). The curvature of the \(T_c\) Vs \(x\) curve changes in the RPr-124 system is unlike that in the RPr-123 system where \(T_c\) Vs \(x\) follows AG theory.

VI.4.3 Abrikosov-Gorkov Theory

In this theory one calculates the transition temperature in the presence of magnetic impurities. The Hamiltonian is

\[
H = H_{\text{BCS}} + \Gamma \vec{S}_c \cdot \vec{S}_i
\]
where \( \vec{S}_e \) and \( \vec{S}_i \) are the spin operators for carrier electron and impurity respectively and \( \Gamma \) the strength of exchange interaction. The second term in above equation is treated as perturbation. One employs the Bogolubov canonical transformation method and evaluates the \( u, v \) coefficients to first order in \( \Gamma \) obtaining for the gap function

\[
\Delta(r) = \int K(r, r') \Delta(r') dr'
\]

where the Kernel \( K(r, r', t) \) is a complicated function of the arguments. It turns out that \( K(t) \) which is called "time-reversal" operators acts differently on up-down electrons of a Cooper pair thus leading to pair breaking. The B.C.S. equation can be written in terms of Fourier transform of \( K(t) \) as

\[
I = N(0)V \int d\xi d\xi' \sum_\omega \frac{KT}{(\xi - i\hbar \omega)(\xi + i\hbar \omega)} \frac{1}{\hbar} g \left[ \frac{\langle \xi - \xi' \rangle}{\hbar} \right]
\]

where

\[
g(\Omega) = \int \frac{dt}{2\pi} < K^+(0) K(t) > e^{-i\Omega t}
\]

For the magnetic impurity problem

\[
\lim_{t \to \infty} < K^+(0) K(t) > = e^{-i\Omega t}
\]

and therefore

\[
g(\Omega) = \frac{1}{\pi} \frac{\tau_K}{1 + \Omega^2 \tau_K^2}
\]

The gap equation becomes

\[
I = N(0)V \sum_\omega 2\pi \frac{KT}{\hbar} \frac{1}{2|\omega| + 1/\tau_K}
\]

The summation over \( \omega \) can be performed using a frequency cut-off at \( \omega_D \) obtaining

\[
I = N(0)V \left[ \ln \left( \frac{1.14\hbar \omega_D}{KT} \right) + \frac{2\pi KT}{\hbar} \times \sum_\omega \left( \frac{1}{2|\omega| + 1/\tau_K} - \frac{1}{2|\omega|} \right) \right]
\]
Fig. VI.6 Transition temperature $T_c$ vs Pr concentration $x$ for the Er-124 system
The sum over $\omega$ can be written in terms of the digamma functions, obtaining finally

$$\ln \left( \frac{T_c}{T_{c0}} \right) = \Psi \left( \frac{1}{2} \right) - \Psi \left( \frac{1}{2} + \frac{\hbar}{4\pi K \tau_K T_c} \right)$$

where $\Psi$ is the digamma function.

The above relation gives the transition temperature $T_c$ in terms of $T_{c0}$, the transition temperature in the absence of impurities and $\tau_K$, the relaxation time (often written as $\tau_{AG}$) related to the resistivity as

$$\frac{1}{\tau_{AG}} = \frac{\eta_0 e^2}{m} \rho_{AG}$$

where $\rho_{AG}$ is the resistivity due to scattering of electrons by impurities. $\tau_{AG}$ can be evaluated by using the interaction term and we finally get

$$\frac{1}{\tau_{AG}} = 2\pi x N_p \Gamma^2(g_J - 1)^2 J(J + 1)$$

where $x$ is the impurity concentration. The quantity $\Gamma^2(g_J - 1)^2 J(J + 1)$ is called de Gennes's factor.

Based on this theory, we calculate $T_c$ for different impurity concentrations $x$. The results of these calculations are shown in Fig. VI.6. It can also be seen from this figure that the AG theory, based on the observed $x_{ci}$ values, is not able to explain the $dT_c/dx$ behaviour in the ErPr-124 system.

On the basis of the above results it is clear that $T_c$ variation in the disordered 124 systems is much more complex than in the 123 systems. While the relative variations of $T_c$ with $x$ in the Y-, Eu- and Er-based 124 systems can be understood on the basis of the different ionic radii of the Y, Er and Eu ions in the system, we need to invoke other ideas to understand the difference in the $T_c$ variation between 123 and 124 systems for a given rare-earth ion.

Both models, viz., hole-filling phenomenology and the Abrikosov-Gorkov pair-breaking theory, which are used to explain the suppression of superconductivity, are not separately valid in this case for the R-124 system (Fig. VI.6). In the following sections we attempt to establish a relation between the observed $T_c$ depression and the AG-theory and the hole-filling model in a phenomenological manner.
VI.4.4 Modified AG Theory

A modification to the AG theory has been suggested by Agarwal et. al [18] by replacing $\rho_{AG}(x)$ in the AG theory by $\rho_0(x)$ - the resistivity due to the impurity. The scattering rate will not vary linearly with $x$. Let $1/\tau_0$ denote the scattering rate corresponding to the resistivity $\rho_0(x)$. Then

$$\frac{1}{\tau_0} = \frac{n_0 e^2}{m} \rho_0(x)$$

Expressing the modification caused by the replacement of $\rho_{AG}(x)$ by $\rho_0(x)$ in terms of an effective impurity concentration $x_{eff}$ by requiring that

$$\frac{1}{\tau_0} = \frac{n_0 e^2}{m} x_{eff} \rho'_AG$$

we get

$$x_{eff} = \rho_0(x)/\rho'_AG$$

Fig. VI.6 shows a plot of $T_c$ values as calculated by modified AG theory versus the Pr concentration $x$. Since we have used the observed values of $\rho_0(x)$ in these calculations, it is not possible to obtain $T_c$ for $x$ values. Though there is a similarity in the trend with the experimental values exact agreement is still lacking. Hence we feel that some further modifications to the AG theory are required.

VI.4.5 Suggested Modifications to the AG theory

We feel that an essential modification to the AG theory is necessary for the following reasons: The AG theory is based on the BCS hamiltonian for a conventional 3D superconductor. Such a Hamiltonian does not explain the properties of a high-$T_c$ superconductor. The anomolous normal state properties are due to strong electronic correlations which are absent in the broad conduction band characterizing the BCS model. Thus a correct starting point must be a model that incorporates two basic features namely strong correlations and two dimensionality. The effect of magnetic impurities can then be calculated using the perturbation theory as done.
Fig. VI.7 X-ray diffraction pattern of ErCe-124 10 at% sample
in the AG theory. Such a model Hamiltonian in the mean field approximation is given by Ruckenstein et al. [47]. It is based on the RVB model in which superconductivity arises as a result of spin correlations due to superexchange between electrons on nearest neighbour Cu sites. The resulting Hamiltonian which correctly reproduces the observed properties of high- $T_c$ superconductors has the BCS form as is given by

$$H_{BCS} = \sum_{k,\sigma} \xi(k)f^{+}_{k,\sigma}f_{k,\sigma} - I \sum_{k} \tau(K)(\Delta f_{-k}f_{k} + H.C.)$$

where

$$\tau(k) = 2[\cos(k_xa) + \cos(k_ya)]; \quad a = \text{lattice spacing}$$

$$\xi(k) = -\delta tr(k) + \text{const.}$$

$$I = 4J(1+\delta) - V$$

where $t$ is the hopping energy, $J$ is the superexchange interaction, $V$ is the nearest neighbour coulomb interaction and $\delta$ is the parameter $0 \leq \delta \leq 1$ that ensures absence of double occupancy.

As is obvious from these expressions there are several adjustable parameters in this theory. These are to be determined from the experimental data on various quantities. Otherwise the main arguments of the AG theory will hold but a new expression for $T_c$ will emerge which can be compared with the data.

### VI.4.6 Superconductivity of the Ce-doped ErBa$_2$Cu$_4$O$_8$ system

We now examine the influence of the substitution of Ce$^{4+}$, in place of Er$^{3+}$, on the superconducting behaviour of ErBa$_2$Cu$_4$O$_8$. Ce was particularly chosen as a substituent in the present study because it is known that Ce does not form the 124 structure and there are very few reports in literature on the study of the influence of Ce$^{4+}$ as a dopant in the 124 phases.

The X-ray diffraction patterns of the 10 at.% Ce-doped Er—124 sample is presented in Fig.VI.7. As can be seen, only upto 10 at% Ce could be
Fig. VI. 8 R-T curve for the ErCe 10 at.% 124 sample
Fig. VI. 9  LIII edges of Er in ErCe –124
substituted at the Er sites in \( \text{ErBa}_2\text{Cu}_4\text{O}_8 \) and the material begins to phase separate for \( x > 0.1 \).

The normalized resistance behaviour for \( \text{Er}_{0.9}\text{Ce}_{0.1}\text{Ba}_2\text{Cu}_4\text{O}_8 \) is shown in Fig.VI.8. The electrical resistance plot shows a knee with the main resistance drop occurring at about 50K, but the sample shows no superconducting behaviour down to 20K. This knee is probably due to an inhomogeneous distribution, implying that the insertion of Ce\(^{4+} \) at the Er-sites is sluggish. The extrapolation of the initial drop in the \( R(T) \) plot (Fig.VI.8), however, hinted that the \( T_c \) value would improve upon reacting for longer periods aimed at a more complete and homogenous of the Ce-ions at the Er-sites. Further sintering has been shown to increase \( T_c \) in some reports [48].

The \( T_c \) depression due to substitution of 10 at% Ce at the Er-sites in the Er-124 system is larger than the magnetic, pair-breaking effect of Pr in the Er-124 and Y-123 systems. The rate of depression of \( T_c \) in c-axis oriented film specimens of the \( \text{Y}_{1-x}\text{M}_x\text{Ba}_2\text{Cu}_3\text{O}_7 \) system for the tetravalent Ce ion is very similar to that for \( M = \text{Pr} \) as observed by Maple et. al. [49]. They argued that the observed depression of \( T_c \) with \( x \) in \( \text{Y}_{1-x}\text{M}_x\text{Ba}_2\text{Cu}_3\text{O}_7 \) (\( M = \text{Ce} \)) can only be accounted for by hole-filling, since there can be no pair-breaking contribution as tetravalent Ce ions have closed shells.

In view of the supposedly fixed oxygen content of the 124-structure, the substitution of Ce\(^{4+} \) is expected to reduce the hole content, and consequently cause a drop in the \( T_c \) values of \( \text{ErBa}_2\text{Cu}_4\text{O}_8 \). Fig.VI.9 shows the \( \text{L}_{III} \) absorption edges of Er in \( \text{ErBa}_2\text{Cu}_4\text{O}_8 \) and \( \text{Er}_{0.9}\text{Ce}_{0.1}\text{Ba}_2\text{Cu}_4\text{O}_8 \). As in the case of the Pr-substituted Er-124, the Er edges are found to be characteristic of trivalent Er, and once again we conclude that the Er valence is not affected by the addition of Ce.

Addition of 10 at% Ce acts as an equivalent of the application of negative pressure on the Er-124 lattice. The unit cell dimensions \( a, b, \) and \( c \) for \( \text{YBa}_2\text{Cu}_4\text{O}_8 \) have been reported to decrease monotonically with the application of external pressure [50,51]. Substitution of Ce\(^{4+} \), too, decreases the parameters \( a \) and \( b \) for \( \text{ErBa}_2\text{Cu}_4\text{O}_8 \) but the cell volume is not affected significantly due to a contraction of the \( c \)-parameter (Tab.VI.1), possibly the influence of the substitution of a more electropositive Ce\(^{4+} \) at the Er-sites.

Attention has been focussed on the relationship between \( T_c \) and the structural dimensions of \( \text{YBa}_2\text{Cu}_4\text{O}_8 \), in particular the basal-plane copper-to-apical-oxygen bond-length, \( \text{Cu}(2)-\text{O}(4) \), which shows a reduction with
the application of pressure [50,51]. It would, therefore, be interesting to examine the influence of substitution of Ce$^{4+}$ on the Cu(2)-O(4) distance and other related structural parameters, such as the chain-apex Cu(1)-O(4) bond length etc., in order to obtain a better understanding of the role of the Cu bond valence in the superconducting behaviour of the 124-phase.
Table VI.1 a, b and c parameters for the Pr- and Ce-doped Er-124 samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErBa$_2$Cu$_4$O$_8$</td>
<td>3.8366</td>
<td>3.8685</td>
<td>27.230</td>
<td>78.50</td>
</tr>
<tr>
<td>(Er$<em>{0.9}$Pr$</em>{0.1}$)Ba$_2$Cu$_4$O$_8$</td>
<td>3.8440</td>
<td>3.8900</td>
<td>27.197</td>
<td>54/55</td>
</tr>
<tr>
<td>(Er$<em>{0.8}$Pr$</em>{0.2}$)Ba$_2$Cu$_4$O$_8$</td>
<td>3.8440</td>
<td>3.8880</td>
<td>27.211</td>
<td>51.00</td>
</tr>
<tr>
<td>(Er$<em>{0.6}$Pr$</em>{0.4}$)Ba$_2$Cu$_4$O$_8$</td>
<td>3.8640</td>
<td>3.8900</td>
<td>27.277</td>
<td>30/35</td>
</tr>
<tr>
<td>(Er$<em>{0.4}$Pr$</em>{0.6}$)Ba$_2$Cu$_4$O$_8$</td>
<td>3.8840</td>
<td>3.8980</td>
<td>27.142</td>
<td>00.00</td>
</tr>
<tr>
<td>(Er$<em>{0.9}$Ce$</em>{0.1}$)Ba$_2$Cu$_4$O$_8$</td>
<td>3.8380</td>
<td>3.8910</td>
<td>27.188</td>
<td>-</td>
</tr>
</tbody>
</table>
References


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