Creation of the Best Performance Superconductor
- based on Cu-1234 with High T_c, J_c, and H_{irr} -

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The best performance superconductor has to have the highest J_c, and H_{irr} and the lowest surface resistance R_s at 77 K. Cu-1234 ($CuBa_2Ca_3Cu_4O_{12-y}$) has four CuO_2 superconducting layer, a conductive CuO_{2+y} charge reservoir layer and a peculiar electronic structure for the performance. The Cu-1234 has a high T_c >117 K (= one and a half time of 77 K) even in over-doping region, a low superconducting anisotropy (γ =1.6), a long coherence length along c-axis (ξ_c = 1 nm) and a small penetration depth (λ_c = 220 nm). Therefore, it is capable of becoming the best performance superconductor with a high J_c {50 M A/cm^2 (77 K, 0 T), 0.5 M A/cm^2 (77 K, 10 T)}, a high H_{irr} {30 T(77 K) }and a low R_s {30 $\mu\Omega$(77 K, 10 GHz) }. These superconducting properties are derived from its unique composition, lattice structure and electronic structure. The prediction is going to be proved with the experimental data of T_c, J_c, H_{irr} and hole concentration, NMR, specific heat and XPS measurements and band calculation. Sustainable high T_c (>117 K) in over doped Cu-1234 were achieved by the selective over-doping effect. Moreover high T_c's of 132 K in $Cu_{1-x}Tl_x$–1223 and 126 K in $Cu_{1-x}Tl_x$–1234 were attained by homogeneous optimum-doping effect.

The thin film preparation methods of Cu-1234 and -1223 systems have been developed by applying a new technique of Tl-assisted APE(amorphous phase epitaxy) method for $Cu_{1-x}Tl_x$-1234 and -1223 system. The thin films of $Cu_{1-x}Tl_x$–1223 have given a high J_c =20 M A/cm^2 (77 K, 0 T) and =0.4 M A/cm^2 (77 K, 10 T) and its data extrapolate a high $(H_{irr})_\perp$~30 T at 77 K. Another new thin film preparation technique for Cu-1234 is developed as SAE(self assembling epitaxy) method by using physical and chemical effects such as sputter deposition, surface diffusion, strict lattice-matching and structure stabilizer.

1. Introduction

Purpose of this project is the creation of the best performance superconductor (Table 1) at 77 K on the basis of the Cu-1234 ($CuBa_2Ca_3Cu_4O_{12-y}$) system.[1-7] Well-known high-T_c superconductors such as Y-123 and Bi-2223 are not enough to satisfy the necessary conditions in irreversible field (H_{irr} >30 T) and surface resistance (Rs <100 $\mu\Omega$ (10GHz)) at 77 K for high field SMES and high sensitive and high power microwave devices. That is caused by their high superconducting anisotropy(γ >5), low H_{irr}(< 10 T at 77 K) and large penetration depth along the c-axis (λ_c > 700 nm). Those are fatal weak-points of high-T_c superconductors for large scale applications and industry such as energy super-highway(=Global Electric Power Superconducting Cables)[8] which demands a large scale SMES, and materials super-highway(=Vacuum Linear-Motor Car) as well as advanced information super-highway.

The fatal weak-points of preexisted high Tc superconductors. originate from a high superconducting anisotropy due to their composition, lattice structure and electronic structure. The high superconducting anisotropy(γ) comes from a short coherence length along the c-axis ξ_c ($\gamma = \xi_{ab}/\xi_c$) and it leads to reduce irreversible field H_{irr} (~H_{c2}/γ^2).[5] The short ξ_c are related to nonconductive charge reservoir layer in Bi-, Tl- and Hg-systems and thin superconducting layer (two CuO_2 layers) in Y-123 systems. Therefor we started to search for new low anisotropic high-Tc superconductors with conductive charge reservoir layer and thick superconducting layer. Then we have discovered a low anisotropic superconductor Cu-1234 with high Tc.[1-3]

Table. 1 The Best performance superconductor

I. Why the best performance superconductor is necessary ?
1. **To solve the EEE & E problems.**
2. **For energy, information and material super highway.**
3. **Bi- and Y-systems have not enough irreversible field (H_{irr} <10 T) at 77 K.**
4. **USA and EU gave up large scale SMES in 1993.**
5. **Low surface resistance (Rs) for high sensitive and high power microwave device.**

II. What is the best performance superconductor ?
1. **High Tc, high Jc, high H_{irr} and low Rs: (H_{irr} ~H_{c2}/γ^2)**
2. **Low anisotropic superconductor($\gamma = \xi_{ab}/\xi_c$), long coherence length(ξ_c). Short penetration depth(λ_c)**
3. **Thick superconducting $(CuO_2)_n$ layer, conductive charge reservoir layer and over-doping state with high Tc.**
4. **Electronic structure for high Tc by selective over-doping and homogenous optimum doping.**
5. **Cu-1234 (>Cu-1245> Cu-1223 > Cu-1212: Y-123)**

III. How is the best performance superconductor prepared ?
1. **High pressure synthesis → Normal pressure synthesis. Artificial catalysis method, SPE(Solid Phase Epitaxy)**
2. **APE (Amorphous Phase Epitaxy) method: Grain boundary diffusion; T~T_m(3/4)**
3. **SAE (Self Assembling Epitaxy) method: Surface diffusion; T~T_m/2**
4. **Introduction of columnar defects for pinning centers Nano-defects ~ ξ : Nano-technology**

IV. When is the best performance superconductor realized?
1. **Physical problems are solved in principle in 2000.**
2. **Fundamental Engineering problems (fabrication) will be solved till 2002 in priciple.**
3. **Economic problems (cost) will be solved till 2003 partly.**

V. What is the next ?
1. **Identification of superconducting symmetry: d → d+is-wave or $d(x^2-y^2)+id(xy)$-wave**
2. **Search for room temperature superconductors: Tc~ 400 K, Low anisotropy and d+is or d+id-wave**

2. Characteristic features of Cu-1234 : Crystal structure and Electronic structure

The superconducting anisotropy γ is defined by the ratio of anisotropic coherence length or of penetration depth as $\gamma = \xi_{ab}/\xi_c = \lambda_c/\lambda_{ab}$. Then ξ_c should be elongated and λ_c should be reduced. The following three conditions are necessary for that. (1) The first condition is the metallic conductive charge reservoir layer, because the coherence length is proportional to Fermi velocity ($\xi \sim hv_F/kT_c$) from the uncertainty principle.[4] The metallic charge reservoir layer should be realized with CuO_{2+y} layer itself. This is effective to reduce effective mass m* and then penetration depth λ_c. (2) The second condition is thick superconducting layer, because the coherence length ξ is limited by the variation of electron coordination ($\xi \sim \Delta x$) from the uncertainty principle ($\Delta x \Delta p \sim h$). The upper limit of coherence length along the c-axis will be proportional to the number of superconducting CuO_2 layers (n>1) by following the equation of ξ_c =0.32(n-1) nm.[4] (3) The third condition is the over-doping state with high Tc, because penetration depth is inversely proportional to square root of charge density n ($\lambda = (m^*/\mu_0 ne^2)^{1/2}$

Thus the Cu-based superconductor family ($CuBa_2Ca_{n-1}Cu_nO_{2n+4-y}$: n=1~15) is a promising candidate for the low anisotropic superconductor. This family is, however, very difficult to synthesize except for n=2 member (Cu-1212, that is Y-123 with the substitution of Y for Ca). Those are synthesized for the first time by high pressure technique.[1,2] Their crystal structures give expected characteristic features as shown in Fig. 1.[9]

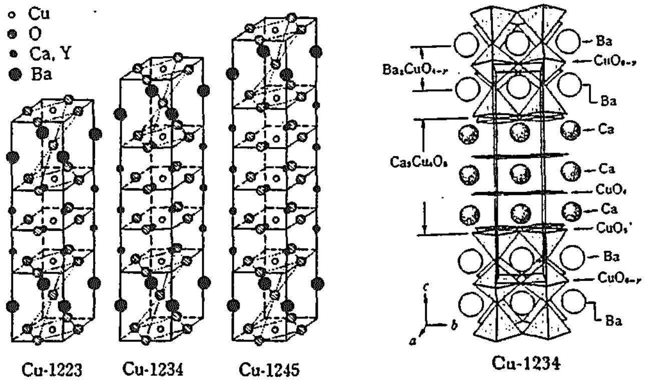

Fig. 1. Crystal structures of ($CuBa_2Ca_{n-1}Cu_nO_{2n+4-y}$: n=3~4) and Cu-1234

At first we have examined the possibility of Cu-1234 as the best performance superconductor. The Cu-1234 consists of thick (0.96 nm) superconducting $Ca_3Cu_4O_8$ layer with four CuO_2 planes and conductive charge-reservoir layer Ba_2CuO_{4-y}. Extreme over-doping state up to 0.8/CuO_2 is possible in Cu-1234 due to the reduction of O-vacancy (y=0 and z=2.8). Homogeneous optimum doping state 0.2/CuO_2 for maximum-Tc is possible with y=1.5 and z=2.2 in Cu-1234 (n=4).

The electronic structure of Cu-1234 is expected as in the model of Fig. 2.[6] The four CuO_2 planes give four bands (band-1, 2, 3 and 4). The four bands, however, split into doubly-degenerated upper bands in over-doped state from outer CuO_2 planes with apical oxygen and doubly-degenerated lower bands in optimum-doped state from inner CuO_2 planes. The density of states(DOS) are obviously different for the both types of band, the one partial DOS is high and the other is low. The electronic structure can give two important possibilities. One is a selective over-doping effect to sustain high-Tc to keep two bands over-doping and other two band optimum-doping in the over-doping region. The other is a homogeneous optimum doping effect to achieve maximum Tc. The modification of electronic structure can give the necessary conditions for the best performance superconductor by controlling the doping level.

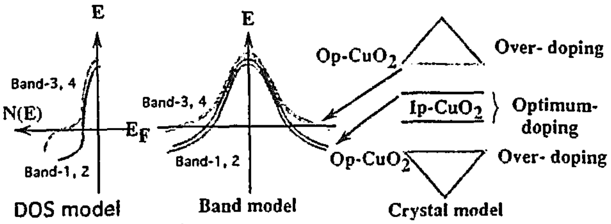

Fig. 2. Electronic structure model of Cu-1234

The band structure of Cu-1234(O_{11}) for y=1 and z=2.4 calculated by FLAPW method shows four bands(band-1, 2, 3 and 4) from four CuO2 planes (Fig. 3).[10, 11] The four bands, however, split into doubly-degenerated lower bands (band-1and 2) in optimum -doped state and doubly-degenerated upper bands (band-3 and 4) in over-doped state. The lower two bands come from inner CuO_2 planes without apical oxygen and the upper two bands from outer CuO_2 planes with apical oxygen. The former have 2d-like cylindrical Fermi surface and large nesting effect, the latter have 3d-like Fermi surfaces and van Hove singularity. The conductive charge-reservoir layer Ba_2CuO_{4-y} gives a single conductive band(-5) crossing the Fermi level which contributes to high Fermi velocity along the c-axis.

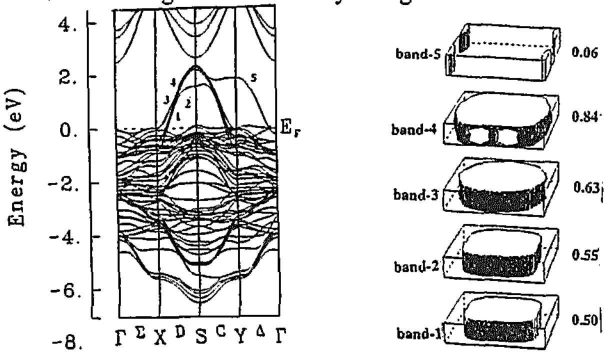

Fig. 3. Band structure and Fermi surfaces of Cu-1234(O_{11}).

3. Low superconducting anisotropy γ, long coherence length ξ_c and short penetration depth λ_c of Cu-1234

The most excellent feature of Cu-1234 is low superconducting anisotropy. The superconducting anisotropy, coherence length and penetration depth were determined from the upper critical field and lower critical field measurements.[3] These data give $(H_{c2})_{ab}(0)$ =121 T and $(H_{c2})_c(0)$=195 T. From the relations $(H_{c2})_{ab} = \phi/(2\pi\xi_{ab}^2)$ and $\xi_c/\xi_{ab} = (H_{c2})_c/(H_{c2})_{ab}$, (where φ is the flux quantum), the coherence lengths of ξ_c =16 Å and ξ_c =10 Å are obtained. This coherence length along the c-axis ξ_c =10 Å is the longest one among the high-Tc superconductors with T_c >77 K. The anisotropic parameter is determined as $\gamma = \xi_{ab}/\xi_c = 1.6$. This anisotropy is 1/3 of $\gamma = 5$ approved for Y-123[3]. (Fig. 4)

The lower critical field H_{c1} is determined as 260 and 630 Oe, respectively, after the demagnetization factor correction. From these values we can estimate the penetration depth as λ_{ab} =120 nm and λ_c =220 nm. The anisotropy of $\gamma = \lambda_c/\lambda_{ab} = 1.8$ is nearly equal within experimental erros to γ =1.6 from the coherence length.

The Cu-1234 has the least γ among the high-T_c superconductors with T_c>77 K as shown in Fig. 5.[6] These least anisotropy comes from the longest coherence length ξ_c and the shortest penetration depth λ_c along the c-axis among the cuprate superconductors. It is caused by the strong superconducting coupling between the thick $Ca_3Cu_4O_8$ superconducting layers (t=0.96 nm) mediated by the metallic charge reservoir layer Ba_2CuO_{4-y} and its over-doped carrier.

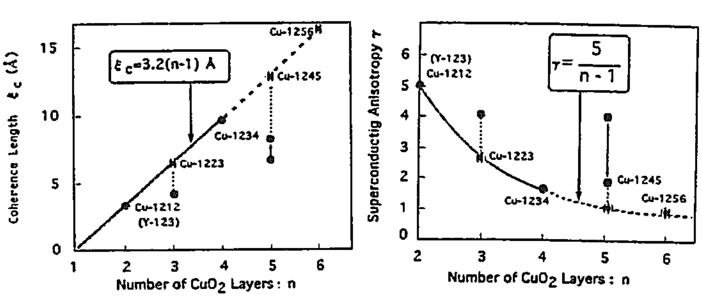

Fig. 4 Coherence length and superconducting anisotropy versus numbers of CuO_2 layer.

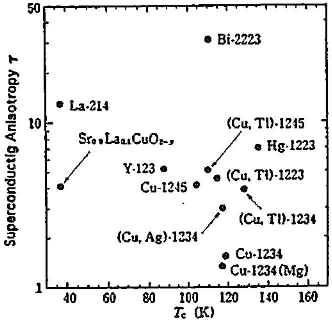

Fig. 5 Superconducting anisotropy vs. Tc for representative High Tc superconductors.

4. High Tc by selective over-doping effect and homogeneous optimum-doping effect

The most outstanding features of Cu-1234 is sustainable high-Tc in the over-doping region. Figure 6 show that Tc can be kept above 117 K even in over-doping region.[12] The mechanism is clarified by the selective over-doping effect based on the hole distribution measurement from the NMR and band calculation. The carrier concentration was determined with consistency by Hall coefficient measurement, iodine titration method and Knight shift from NMR measurement (Fig. 7).[6, 13] The Knight shift of each CuO_2 plane gives the carrier concentration of each CuO_2 plane as shown in Fig. 8.

NMR measurement proved the selective over-doping phenomena microscopically.[13] Difference of hole concentration between the outer plane and inner plane increase with the increase of average hole concentration and the hole concentration in the inner plane is kept as almost constant as shown in Fig. 8. This is consistent with the model of electronic structure in Fig. 2.

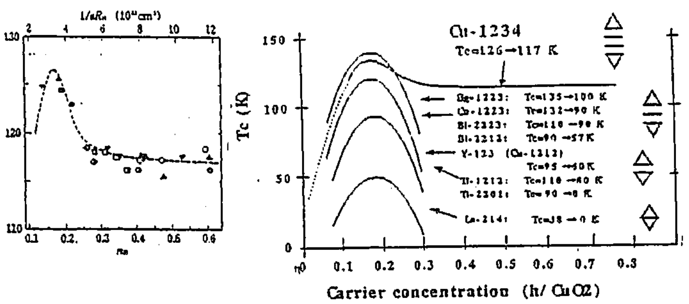

Fig. 6 Tc vs. carrier concentration of Cu-1234 system(a) and. of high Tc superconductors (b).

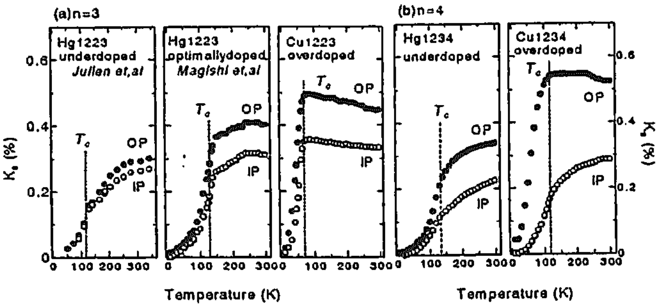

Fig. 7 Knight shifts from NMR measurements.

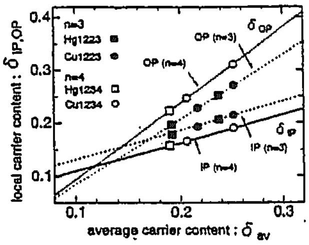

Fig. 8 Carrier concentration in IP (inner plane) and OP (outer plane) of high-Tc superconductors.

Further the band model indicates the possibility of the homogeneous optimum doping for Tc enhancement. This effect is very important for achieving the maximum Tc. This was realized by reducing the role of apical oxygen with the elongation of bond length between Cu and apical oxygen in Cu1-xTlx-1234 system to achieve Tc=126 K[14]. The selective reduction of charge reservoir layer is another way to enhance the Tc.[15,16] Those effects were commonly observed in $Cu_{1-x}Tl_x$–1234 and –1223 systems.[17, 18] High T_c of 132 K in $Cu_{1-x}Tl_x$–1223 were attained by this homogeneous optimum-doping effect.(Fig. 9)

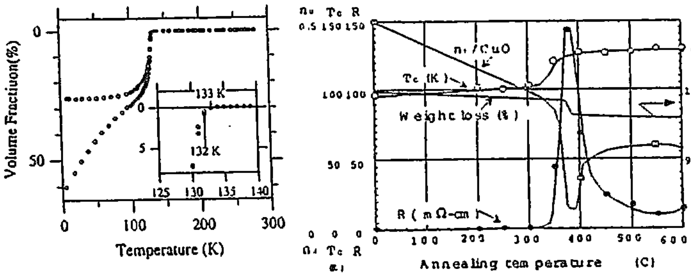

Fig. 9 Tc, resistivity, hole concentration and weight loss versus annealing temperature for $Cu_{1-x}Tl_x$–1223 sample.

The homogeneous optimum-doping mechanism was clarified by XPS measurements (Fig. 10)[18] and band calculation (Fig. 11).[19]

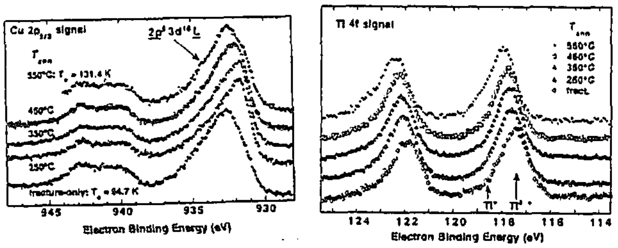

Fig. 11 XPS spectra of heat treated CuTl-1223 sample.

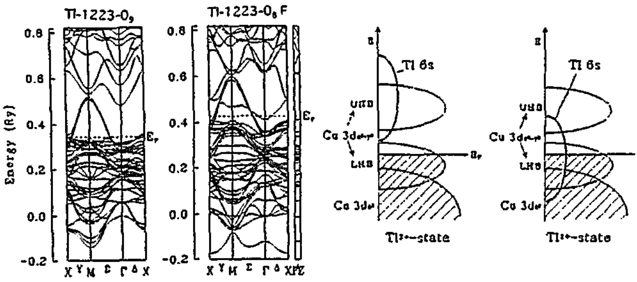

Fig. 11 Band structures of Tl-1223(O_9) and Tl-1223(O_8F).

These results give an empirical rules of T_c [=98+f(n-1)] as a function of the numbers of CuO_2 layers n. (Fig. 12) It predicts a high T_c of 140 K for CuTl-1234 system as shown in Fig. 12.

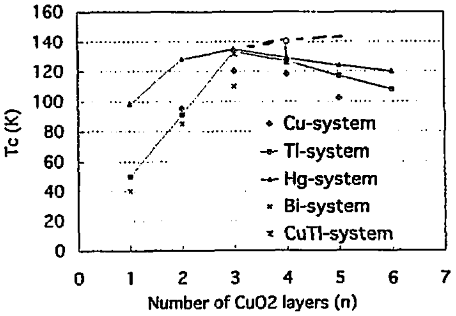

Fig. 12 Relation between Tc and numbers of CuO_2 layer for $Cu_{1-x}Tl_x Ba_2Ca_{n-1}Cu_nO_{2n+4-y}$: n=1~7.

5. Possibility of the best performance superconductor: High J_c , high H_{irr} and low surface resistance R_s

The experimental results of Cu-1234 revealed the low superconducting anisotropy γ =1.6, the long coherence length of ξ_c=1.0 nm and the short penetration depth of λ_c=220 nm. These results indicate high J_c (=H_c/λ) and high H_{irr} (~$H_{c2}(0)/\gamma^2$). These properties of Cu-1234 could be improved by more than a factor of 3 in comparison with Y-123. Further the J_c and H_{irr} values are enhanced by the increase of carrier concentration. The selective over-doping effect in Cu-1234 to keep T_c over 117K would be very useful to enhance the J_c and H_{irr}.

The de-pairing Jc of Cu-1234 is estimated as J_c =300 M A/cm^2 (77 K, 0 T) from the value of H_c = $(H_{c2} H_{c1})^{1/2}$ ~3 T and λ_c=220 nm. H_{irr}(T) is estimated from $(H_{c2})_{ab}$, superconducting anisotropy γ and a temperature dependence factor of [1-(T/T$_c$)^2] as following the formula for T < (4/5) T_c .[5]

$$H_{irr}(T) = H_{c2}(0)\,[1-(T/T_c)^2]\,/\,\gamma^2 \qquad (1)$$

The estimated H_{irr} values of Bi-2223 and Y-123 at 77 K are 0.5 T and 8 T, respectively, which are consistent with experimental values as shown in Table 2. Therefore, 43T of H_{irr} for Cu-1234 are expected as a realizable value at 77 K.

Table 2. Comparison of Superconducting properties among the representative high-Tc superconductors.

Material	Tc (K)	$H_{c2}(0)_{//ab}$ (T)	$H_{c2}(0)_{//c}$ (T)	ξ_{ab} (nm)	ξ_c (nm)	$\gamma = \xi_{ab}/\xi_c$	$H_{irr}(77)_{cal.}$ (T)	$H_{irr}(77)_{exp}$ (T)
Bi-2223	110	900	30	30	1	30	0.5	0.3
Y-123	95	600	120	16	3	5	8	8
Cu-1234	117	195	121	16	10	1.6	43	8 (30)

The thin films of $Cu_{1-x}Tl_x$– 1223 have been prepared by amorphous phase epitaxy (APE) method. The films give high J_c =20 M A/cm^2 (77 K, 0 T) and 0.4 M A/cm^2 (77 K, 10 T which are twice of the maximum values of Y-123 as shown in Fig. 10[5]. The J_c –H curve extrapolate a high $(H_{irr})_\perp$~30 T at 77 K.

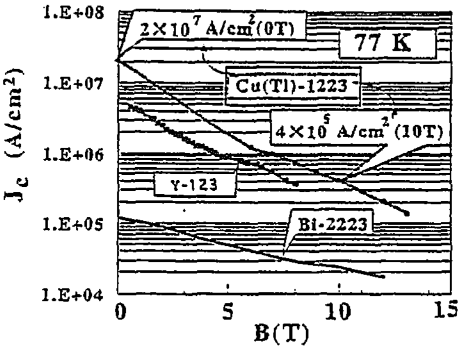

Fig. 13 Jc-H curves at 77 K for thin film $Cu_{0.5}Tl_{0.5}$-1223.

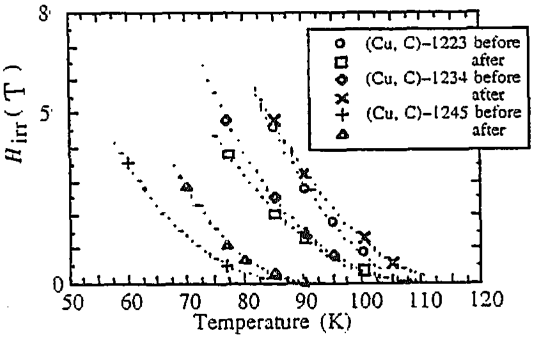

Fig. 14 H_{irr}-T curves for bulk (Cu,C)-1223,1234 and 1245.

The J_c-H curves for a neutron irradiated Cu-1234 sample shows the high H_{irr}=8 T at 77 K for the criterion Jc=1000 A/cm^2.[22]. This value corresponds to the maximum H_{irr} of Y-123. The further enhancement of H_{irr} in Cu-1234 could be possible with the introduction of proper pinning centers such as columnar defects.

The surface resistance R_s (~λ^3) of Cu-1234 would be reduced by small penetration depth, high T_c and high carrier concentration. Comparison with Y-123 gives a small surface resistance of R_s<30 $\mu\Omega$ (10GHz, 77K) for Cu-1234 by taking accounts of R_s=100$\mu\Omega$(10GHz, 77K) of Y-123 and the difference of their T_c. For this purpose the SAE(self assembling epitaxy) method will become an essential technique.[20, 21]

6. Transformation of superconducting symmetry

The performance of superconductor will be more enhanced by reducing the superconducting anisotropy in ab-plane to transform the superconducting symmetry from d-wave to d+is or d(x^2-y^2)+id(xy)-wave as shown in Fig. 15. The simple way for the symmetry transformation is over-doping, because t/U factor and probability of Cooper pairs at on-site ψ(r=0) will be increased by doping and a simple d-wave becomes unstable. The experimetal results of NMR from ^{63}Cu show double Tc's at 117 K and 60 K.[13] The both order parameters are identified as d-wave. The specific heat measurement shows double Tc's at 117 K and around 70 K.[23] These results strongly indicate the possibility of transformation of superconducting symmetry from d to d+is or d+id-wave with low anisotropy in ab-plane.

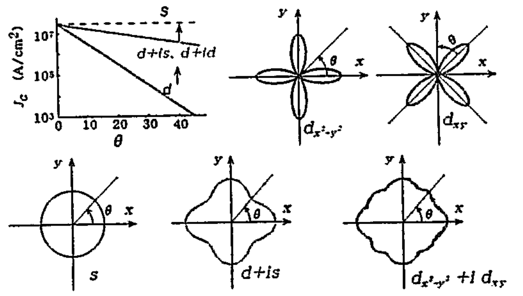

Fig. 15 Jc dependence on crystal junction angle for superconducting symmetries d, d+is, d+id and s-wave.

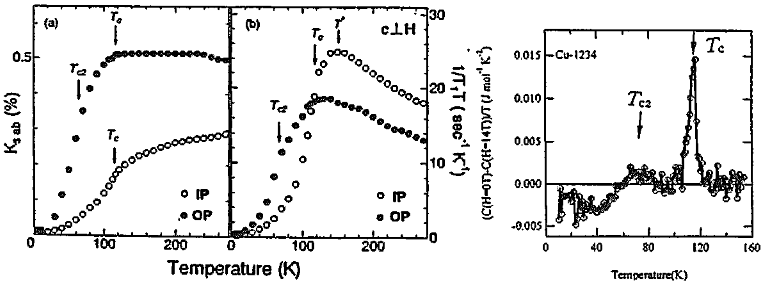

Fig. 16 Double Tc's observation from NMR and specific heat measurements for over-doped Cu-1234.

Summary

Cu-1234 has a high T_c >117 K even in over-doping region, a low superconducting anisotropy (γ=1.6), a long coherence length along c-axis (ξ_c = 1 nm) and a small penetration depth (λ_c = 220 nm). It is capable of becoming the best performance superconductor with a high J_c {50 M A/cm^2 (77 K, 0 T), 0.5 M A/cm^2 (77 K, 10 T)}, a high H_{irr} {30 T(77 K)} and a low surface resistivity {Rs<30$\mu\Omega$(77 K, 10 GHz)}. The physical problems of Cu-1234 system for the best performance superconductor at 77 K have been almost solved, but the material-engineering and economic problems still remain to be solved in the next stage.

Acknowledgements

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