

# Formation temperature of bosons in high- $T_c$ $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ systems

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At different equilibrium temperatures, a precise measurement of the electrical resistivity ( $R$ ) is performed for high  $T_c$  polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  systems.  $T^2$  law is applied in the part of the  $R$ - $T$  relationship far above the superconducting transition temperature. Since Landau and Pomeranchuk predicted the  $T^2$  law arising from electron-electron scattering, a higher critical temperature of  $T^2$  law is defined as a start point ( $T_{\text{es}}$ ) of electron-electron scattering. On the other hand, we defined a lower critical temperature of  $T^2$  law as the formation temperature ( $T_{\text{ee}}$ ) of an electron-electron pair, i.e. the formation temperature of boson.  $T_{\text{ee}}$  relates to the offset temperature of the superconducting transition ( $T_{\text{c,off}}$ ).

## 1. Introduction

Several workers have reported high superconducting transition temperatures above boiling point (b.p.) of  $\text{N}_2$  for the Y-Ba-Cu-O oxide [1-5]. It is important to suggest a new model of superconducting transition. Since an electron-phonon coupling of the BCS model [6] might be partially inapplicable for high  $T_c$  materials, new models, which are suggested to be electron-electron pairs and groups such as an exciton mechanism, have been proposed [7-9]. A law of  $T^2$ , which is the temperature dependence of electrical resistivity, was applied for Li, Na, K and Ag at extremely low temperature [10-12]. Landau and Pomeranchuk predicted the law from electron-electron scattering [13]. If some new models were applied for the high  $T_c$  of the Y-Ba-Cu-O system, the  $T^2$  law would be found at high temperature. We found the  $T^2$  law of the temperature dependence of the electrical resistivity above the onset temperature of the transition for the high  $T_c$  polycrystalline Y-Ba-Cu-O system [14]. We define a lower critical temperature of  $T^2$  law as the formation temperature ( $T_{\text{ee}}$ ) of boson. At  $T_{\text{ee}}$  the electron-electron pair converts to the boson instead of scattering. The purpose of the present work is to investigate the relationship between  $T_{\text{ee}}$  and  $T_{\text{c,off}}$  for the high  $T_c$  polycrystalline Y-Ba-Cu-O system.

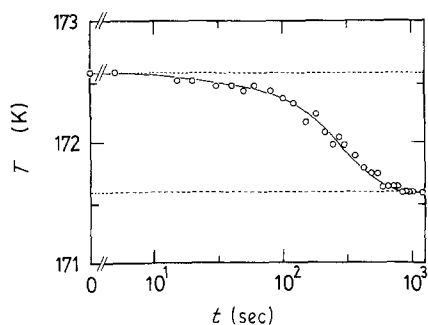


Figure 1 Change in temperature with time. Equilibrium temperature is taken at about 1000 sec.

## 2. Sample preparation

Samples with nominal composition  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  were prepared from high purity powders of  $\text{CuO}$ ,  $\text{BaCO}_3$  and  $\text{Y}_2\text{O}_3$ . The powders were mixed and reacted at 1200 K in air and then air-cooled. After crushing, the pelletized tablet, 2 mm thick, 23 mm diameter, was sintered in air at 1200 K and furnace-cooled. The cooling rate was  $7.0 \times 10^{-2} \text{ K sec}^{-1}$ . Experimental conditions of sample preparation, lattice constants and results are summarized in Table I.

## 3. Electrical resistivity change with temperature

Electrical resistivity was measured using a standard four-probe technique and a Keithley 181 nanovoltmeter. The temperature was measured by Au\*Fe-chromel thermocouple attached to the specimen in a cryostat at equilibrium temperatures. Figure 1 shows temperature change with cooling time. Since the value of the resistivity depends on the scanning rate of the cryostat (see Fig. 2), the most important point is a precise measurement of the electrical resistivity at equilibrium temperatures.

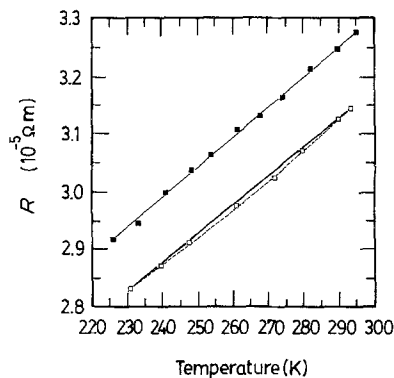


Figure 2 Change in electrical resistivity ( $R$ ) with temperature ( $T$ ) of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system. (□) is for the measurement at equilibrium temperature; (■) is for the measurement on continuous cooling conditions (scanning rate is  $0.12 \text{ K sec}^{-1}$ ).

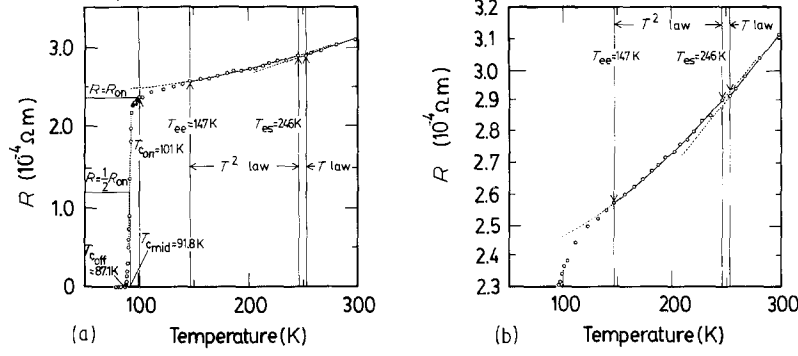


Figure 3 Change in electrical resistivity ( $R$ ) with temperature ( $T$ ) of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system.

Figure 3 shows the temperature dependence of electrical resistivity of the high  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  oxide. The lower the temperature, the lower the electrical resistivity becomes. An apparent deviation occurs at a temperature between 101 and 147 K. There is a sharp drop between 87.1 and 101 K. Offset,  $T_{\text{c,off}}$ , of the transition is defined as the temperature corresponding to the achievement of zero-resistivity (below  $10^{-9} \Omega\text{m}$ ). Onset,  $T_{\text{c,on}}$ , of the transition is defined as the temperature corresponding to the achievement of the deviation of the electrical resistivity. Namely,  $T_{\text{c,on}}$  is taken as the temperature at  $dR/dT = 0.03 \times R^{300\text{K}}$ , where  $dR/dT$  and  $R^{300\text{K}}$  are the slope of  $R-T$  and the resistivity at 300 K, respectively. The midpoint is designated  $T_{\text{c,mid}}$ . The  $T_{\text{c,off}}$  and  $T_{\text{c,mid}}$  values of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system are 87.1 and 91.8 K, respectively.

#### 4. $T^2$ law

It is traditional to express the total electrical resistivity  $R$  as the sum of two terms:

$$R = R_0 + R(T) \quad (1)$$

Here  $R(T)$  is the temperature dependent term arising from the dynamic deviations from crystal perfection.  $R_0$  is the temperature independent residual resistivity arising from the static imperfections, such as impurities and lattice defects.  $R(T)$  relates to temperature ( $T$ ) as in the following equations:

$$R(T) = A_{\text{ep}} T \quad (\text{at high temperature}) \quad (2)$$

$$R(T) = A_{\text{ee}} T^2 \quad (\text{at low temperature}) \quad (3)$$

Here  $A_{\text{ep}}$  and  $A_{\text{ee}}$  are constants. Equation 2 is applied for metals near room temperature and is dominated by electron-phonon scattering. Equation 3 is applied for alkali and noble metals at extremely low temperature [10–12]. Since the effect of the electron-phonon scattering is small at low temperature, Equation 3 is dominated by the electron-electron scattering. Figures 4a and b show change in  $R$  with  $T^2$  for the high  $T_c$  (above 90 K) Y–Ba–Cu–O oxide. Although the temperature is not low, we find that Equation 3 applies far above the superconducting transition temperature. Landau and Pomeranchuk predicted

TABLE I Experimental conditions of sample preparation

Sample no.	Volume fraction (x)	Preparation				Measurement conditions		
		Temp. (K)	Time (h)	FA	CR (K sec <sup>-1</sup> )	Cross-sectional area (m <sup>2</sup> )	CD (A m <sup>-2</sup> )	TD (mm)
A-1	0	1200	(2, 8)	air	$7 \times 10^{-2}$	$3.69 \times 10^{-6}$	271	0.829
A-2	0	1200	(2, 8)	air	$7 \times 10^{-2}$	$3.69 \times 10^{-6}$	271	0.758
A-3	0	1200	(0, 10)	air	$7 \times 10^{-2}$	$4.04 \times 10^{-6}$	1000	0.797
A-4	0	1173	(3, 24)	air	$7 \times 10^{-2}$	$6.01 \times 10^{-6}$	200	0.354
A-5	0	1200	(2, 8)	air	$7 \times 10^{-2}$	$6.08 \times 10^{-6}$	200	1.974
A-6	0	1200	(3, 24)	air	$7 \times 10^{-2}$	$2.55 \times 10^{-6}$	1003	3.812
A-7	0	1200	(3, 24)	air	$7 \times 10^{-2}$	$2.73 \times 10^{-6}$	1004	2.725
A-8	0	1200	(3, 24)	air	$7 \times 10^{-2}$	$2.45 \times 10^{-6}$	1001	6.402
B-1	0.01 (Pd)	1200	(0, 10)	air	$7 \times 10^{-2}$	$4.09 \times 10^{-6}$	200	1.194
B-2	0.005 (Pd)	1200	(0, 10)	air	$7 \times 10^{-2}$	$4.41 \times 10^{-6}$	200	1.359
B-3	0.001 (Pd)	1200	(0, 10)	air	$7 \times 10^{-2}$	$7.76 \times 10^{-6}$	200	0.350
B-4	0.0001 (Pd)	1200	(0, 10)	air	$7 \times 10^{-2}$	$4.48 \times 10^{-6}$	200	0.498
C-1	0.1 (Ti)	1200	(0, 10)	air	$7 \times 10^{-2}$	$6.02 \times 10^{-6}$	200	0.683
C-2	0.01 (Ti)	1200	(0, 10)	air	$7 \times 10^{-2}$	$6.12 \times 10^{-6}$	200	0.681
C-3	0.001 (Ti)	1200	(0, 10)	air	$7 \times 10^{-2}$	$5.54 \times 10^{-6}$	200	0.756
C-4	0.0001 (Ti)	1200	(0, 10)	air	$7 \times 10^{-2}$	$8.07 \times 10^{-6}$	200	0.522
C-5	0.00001 (Ti)	1200	(0, 10)	air	$7 \times 10^{-2}$	$4.56 \times 10^{-6}$	200	1.660
D-1	0	1200	(2, 8)	air	$7 \times 10^{-2}$	$3.69 \times 10^{-6}$	271	0.604
D-2	0	1200	(2, 8)	air	$7 \times 10^{-2}$	$3.69 \times 10^{-6}$	271	0.649
D-3	0	1200	(2, 8)	air	$7 \times 10^{-2}$	$3.69 \times 10^{-6}$	271	0.531

FA; furnace atmosphere

CR; cooling rate

CD; current density

TD; terminal distance

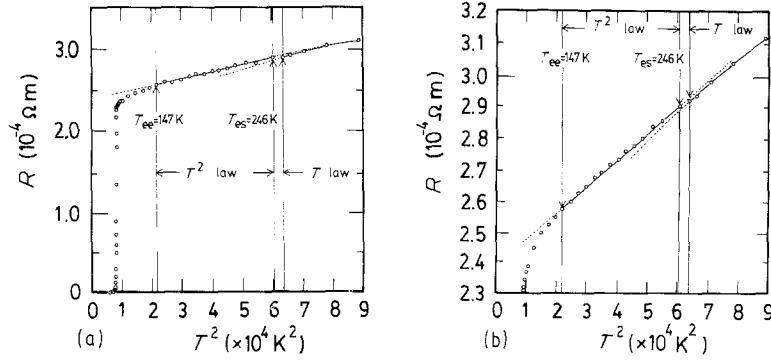


Figure 4 Change in electrical resistivity ( $R$ ) with  $T^2$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system.

Equation 3 arising from the electron–electron scattering [13]. Figure 5a shows a schematic drawing of the scattering. At the same time of the collision of the electrons, both the electrons should be at the same energy level below Fermi level, although the pairing time is short.

If the scanning rate is high (see Figs 1 and 6) as usually occurs, the  $T^2$  law cannot be found and Equation 2 is applied just above the superconducting transition. Therefore, the most important point at which to measure the electrical resistivity is at equilibrium temperature.

## 5. Formation temperature ( $T_{ee}$ ) of boson

Figure 5b shows a schematic drawing of the electron–electron pairing. The electron–electron pair (fermion) converts to boson at  $T_{ee}$  in Figs 3 and 4, although the electron–electron scattering is found above  $T_{ee}$ . Figure 5c shows a schematic drawing of the boson far below  $T_{ee}$  near  $T_{c\text{off}}$ . Many bosons form at  $E_0$  of energy level. Thus, the  $R$  change does not apply for the  $T^2$  law below  $T_{ee}$  (see Fig. 4). If  $T_{ee}$  is the formation temperature of a boson,  $T_{ee}$  change should agree with  $T_c$  change.

In other words, the higher the  $T_{ee}$ , the higher the  $T_c$  may become.  $T_{ee}$  is summarized in Table II.

Figure 7 shows the  $T_{c\text{off}}$  change with  $T_{ee}$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  systems in various conditions [15–18]. The higher the  $T_{ee}$ , the higher the  $T_c$  becomes. Although the work was investigated by use of different kinds of  $\text{CuO}$  powders under different heat treatments, the  $T_{c\text{off}}-T_{ee}$  relation may be applied as a general rule.  $T_{c\text{off}}$  is expressed by the following equation:

$$T_{c\text{off}} = 0.087T_{ee} + 74.9 \quad (4)$$

Figure 8 shows  $T_{ee}$  change with Pd and Ti additions. The small amount of added solutes increases  $T_{ee}$ . The maximum  $T_{ee}$  for Pd and Ti is 190 and 204 K at  $x = 10^{-3}$ , respectively (where  $x$  is the volume fraction added). We have investigated the effects of Pd and Ti additions on  $T_{c\text{off}}$  [16, 17]. Figure 9 shows change in  $T_{c\text{off}}$  with Pd and Ti additions. Small amounts of Pd and Ti additions increase  $T_{c\text{off}}$ . The maximum  $T_{c\text{off}}$  for Pd and Ti are 92.0 and 93.0 K at  $x = 10^{-3}$ , respectively. Excess additions of Pd and Ti decrease  $T_{c\text{off}}$ . The  $T_{ee}$  change is consistent with the  $T_{c\text{off}}$  change. Figure 10 shows  $T_{c\text{off}}$  change with  $T_{ee}$ .  $T_{c\text{off}}$  is expressed by the

TABLE II Results of off set temperature ( $T_{c\text{off}}$ ), formation temperature of boson ( $T_{ee}$ ) and lattice constant

Sample no.	$T_{c\text{off}}$ (K)	$T_{ee}$ (K)	X-ray diffraction analysis				
			CS	Lattice constant (nm)			OC
				$a$	$b$	$c$	
A-1	89.2	165	-	-	-	-	-
A-2	89.0	164	-	-	-	-	-
A-3	88.0	158	ortho	0.3895	0.3823	1.1684	6.79
A-4	87.1	147	ortho	-	-	-	-
A-5	92.0	190	ortho	0.3894	0.3830	1.1712	6.66
A-6	86.5	130	-	-	-	-	-
A-7	85.8	122	-	-	-	-	-
A-8	90.4	181	-	-	-	-	-
B-1	87.0	122	ortho	0.3895	0.3825	1.1686	6.88
B-2	90.0	180	ortho	0.3893	0.3826	1.1678	6.82
B-3	92.0	190	ortho	0.3876	0.3811	1.1629	6.88
B-4	89.0	190	ortho	0.3883	0.3818	1.1649	6.96
C-1	79.0	108	ortho	0.3891	0.3833	1.1672	6.85
C-2	91.0	173	ortho	0.3888	0.3820	1.1665	6.89
C-3	93.0	204	ortho	0.3889	0.3823	1.1666	6.88
C-4	90.0	176	ortho	0.3893	0.3826	1.1679	6.82
C-5	89.0	167	ortho	-	-	-	-
D-1	90.3	168	-	-	-	-	-
D-2	91.5	171	-	-	-	-	-
D-3	93.7	181	-	-	-	-	-

CS; crystal structure; OC; oxygen content.

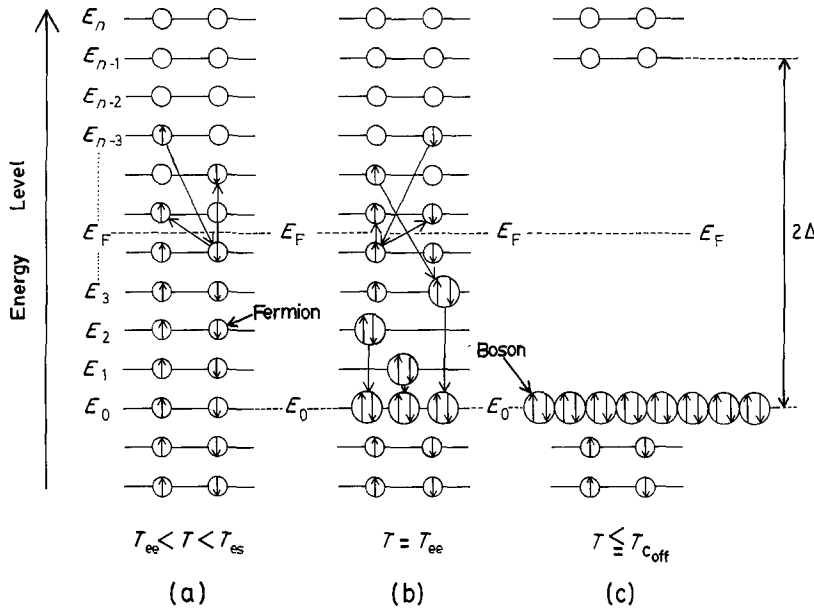


Figure 5 Schematic model of fermion and boson. (a) Electron-electron scattering between  $T_{ee}$  and  $T_{ee}$  in Fig. 3, (b) model at lower critical temperature ( $T_{ee}$ ; formation temperature of boson) of  $T^2$  law, (c) model below  $T_{c_{off}}$ .

following equation:

$$T_{c_{off}} = 0.113T_{ee} + 69.9 \quad (5)$$

The slope and constant of Equation 5 are similar to those of Equation 4.

We have studied  $T_{c_{off}}$  change with stress [18]. The stress increases  $T_{c_{off}}$ . Thus, we show the relationship between  $T_{c_{off}}$  and  $T_{ee}$ , too, see Figure 11. The higher the  $T_{ee}$ , the higher the  $T_{c_{off}}$  becomes, too.  $T_{c_{off}}$  is expressed

by the following equation:

$$T_{c_{off}} = 0.276T_{ee} + 43.9 \quad (6)$$

The slope of Equation 6 is about  $2.7 \pm 0.4$  times larger than that of Equations 4 and 5. This shows that the effects of both the stress and solutes is not completely same, although the  $T_{ee}-T_{c_{off}}$  law is applied as a general principle for the high  $T_c$   $YBa_2Cu_3O_{7-y}$  system. The results are consistent with the assumption that  $T_{ee}$  is the formation temperature of a boson.

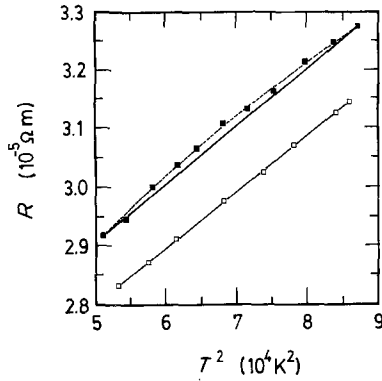


Figure 6 Change in electrical resistivity ( $R$ ) with  $T^2$  of  $YBa_2Cu_3O_{7-y}$  system. ( $\square$ ) is for the measurement at equilibrium temperature: ( $\blacksquare$ ) is for the measurement under continuous cooling conditions (scanning rate is  $0.12 \text{ K sec}^{-1}$ ).

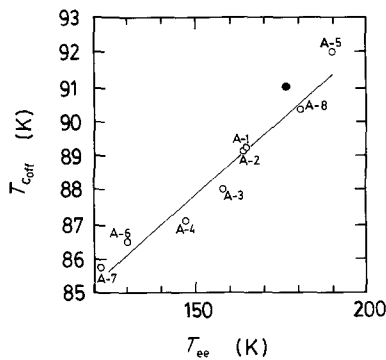


Figure 7 Relationship between offset temperature ( $T_{ee}$ ) of  $T^2$  law of  $YBa_2Cu_3O_{7-y}$  system. ( $\bullet$ ) is for an oxygen processed sample.  $T_{c_{off}} = 0.087$ ,  $T_{ee} = 7.49 \text{ K}$ .  $86 \text{ K} < T_{c_{off}} < 92 \text{ K}$ ,  $122 \text{ K} < T_{ee} < 190 \text{ K}$ .

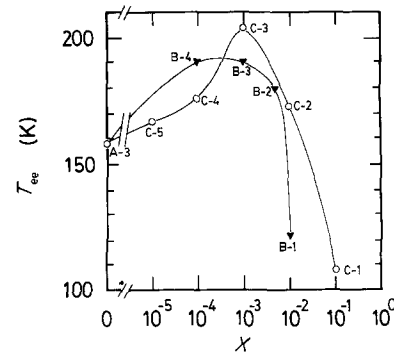


Figure 8 Change in lower critical temperature ( $T_{ee}$ ; formation temperature of boson) of  $T^2$  law with ( $\circ$ ) Ti and ( $\blacktriangledown$ ) Pd volume fraction ( $x$ ) of  $YBa_2(Cu_{1-x}Pd_x \text{ or } Ti_x)_3O_{7-y}$  system.

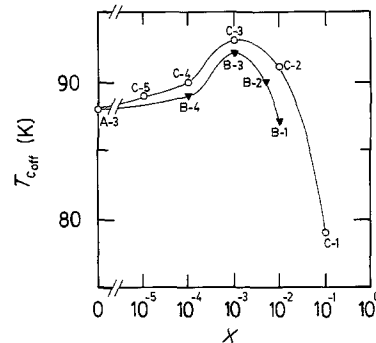


Figure 9 Change in offset temperature ( $T_{c_{off}}$ ) of superconducting transition with ( $\circ$ ) Ti and ( $\blacktriangledown$ ) Pd volume fraction ( $x$ ) of  $YBa_2-(Cu_{1-x}Pd_x \text{ or } Ti_x)_3O_{7-y}$  system.

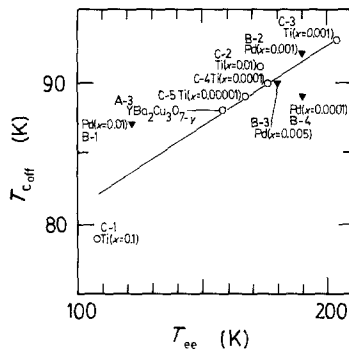


Figure 10 Relationship between offset temperature ( $T_{c\text{off}}$ ) of  $T^2$  law of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Pd}_x$  or  $\text{Ti}_x)_3\text{O}_{7-y}$  system.  $T_{c\text{off}} = 0.113 T_{ee} + 69.9 \text{ K}$ .  $79 \text{ K} < T_{c\text{off}} < 93 \text{ K}$ .  $108 \text{ K} < T_{ee} < 204 \text{ K}$ .

## 6. Conclusion

We investigated a lower critical temperature of  $T^2$  law as the formation temperature of a boson for the high  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system, where the electrical resistivity is measured at different equilibrium temperatures. The higher the  $T_{ee}$ , the higher the  $T_{c\text{off}}$  becomes. Therefore, we suggest that the  $T_{ee} - T_{c\text{off}}$  law is applied as a general principle for the high  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system.

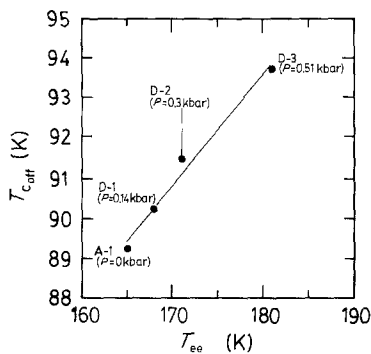


Figure 11 Relationship between offset temperature ( $T_{c\text{off}}$ ) and lower critical temperature ( $T_{ee}$ ) of  $T^2$  law of compressed  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  system.  $T_{c\text{off}} = 0.276 T_{ee} + 43.9 \text{ K}$ .  $89 \text{ K} < T_{c\text{off}} < 94 \text{ K}$ .  $165 \text{ K} < T_{ee} < 181 \text{ K}$ .

## References

1. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MERG, L. GAO, Z. J. HAUNG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
2. J. Z. SUN, D. J. WEBB, M. NAITO, K. CHAR, M. R. HAHN, J. W. P. HSU, A. D. KENT, D. B. MITZI, B. OH, M. R. BEASLEY, T. H. GEBALLE, R. H. HAMMOND and A. KAPITULNIK, *ibid.* **58** (1987) 1574.
3. Y. ZHONGJIN, Z. NAIPING, J. XIAOPING, P. DEXING, Q. HONGBO, S. GUOYUE, Z. ZE and Y. HUAFENG, *J. Phys. C* **20** (1987) L351.
4. S. B. QADRI, L. E. TOTH, M. OSOFSKY, S. LAWRENCE, D. U. GUBSER and S. A. WOLF, *Phys. Rev. B* **35** (1987) 7235.
5. J. M. TARASCON, W. R. MCKINON, L. H. GREENE, G. W. HULL and E. M. VOGEL, *ibid.* **36** (1987) 226.
6. J. BARDEEN, L. N. COOPER and J. R. SCHRIEFER, *Phys. Rev.* **108** (1957) 1175.
7. C. M. VARMA, S. SCHMITT-RINK and E. ABRAHAMS, *Solid State Commun.* **62** (1987) 681.
8. W. Y. CHING, Y. XU, G. L. ZHAO, K. W. WONG and F. ZANDIEHNADAM, *Phys. Rev. Lett.* **59** (1987) 1333.
9. P. W. ANDERSON, *Science* **235** (1987) 1196.
10. G. KRILL, *Solid State Commun.* **9** (1971) 1065.
11. B. LEVY, M. SINVANI and A. J. GREENFIELD, *Phys. Rev. Lett.* **43** (1979) 1822.
12. M. KHOSHNEISAN, W. P. PRATT Jr, P. A. SCHROEDER, S. STEENWYK and C. UHER, *J. Phys. F* **9** (1979) L1.
13. L. LANDAU and I. POMERANCHUK, *Phys. Z. Sowjet.* **10** (1936) 649.
14. Y. NISHI, A. IGARASHI, S. TOKUNAGA and S. MORIYA, *J. Mater. Sci. Lett.* **7** (1988) 649.
15. Y. NISHI, unpublished data.
16. Y. NISHI, S. MORIYA and S. TOKUNAGA, *J. Mater. Sci. Lett.* **7** (1988) 359.
17. *Idem*, *Phys. Lett. A* **126** (1987) 55.
18. Y. NISHI, N. NINOMIYA and S. TOKUNAGA, *J. Mater. Sci. Lett.* **7** (1988) 361.

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