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Final Report to
Office of Naval Research

Period covered: April 1st, 1988 through Sep. 1st, 1989.

Contract No.: N00014-88-K-0283

RT No.: 4128010 --- 01/03 FEB 1988/1112

Title of Project: Experiments on single-crystals of the high Tc oxides $YBa_2Cu_3O_{7-y}$ and $La_{2-x}Sr_xCuO_4$.

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Office of Naval Research

Publications/Patents/Presentations/Honors Report

FINAL REPORT

Period	April 1st, 1988 through Sep. 30th, 1989
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Principal Investigator:	Professor N. Phuan Ong
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a. Number of papers submitted to refereed journals but not yet published: 0

b. Number of papers published in refereed journals: (1988 though Sep. 89) 11

c. Number of books or chapters submitted but not yet published: 0

d. Number of books or chapters published: 7

e. Number of technical reports and non-refereed papers: 0

f. Number of patents filed: 1 (1989)

g. Number of patents granted: 0

(Patent No. 4,996.186 entitled *Flux Method for producing crystals of* $YBa_2Cu_3O_7$ was awarded by the U.S. Patent and Trademark Office, Feb. 26th, 1991.)

h. Number of invited presentations at workshops or professional meetings: 7

i. Number of presentations at workshops or prof. society meetings: 3

j. Honors/Awards/Prizes: 0

k. Total number of graduate students and post docs supported at least 25 % this year on contract

graduate students	4,	post-docs	2
grad student female	0,	post doc female	0
grad stu minority	0,	post doc minority	0

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Statement A per telecon Richard Brandt
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List of publications supported by Office of Naval Research

Contract N 00014-88-K-0283 (Period Apr. 1st, 1988 through Sep. 30th, 1989).

Publications in refereed journals.

1) Z.Z. Wang and N.P. Ong, "Anisotropic thermopower in single crystal $YBa_2Cu_3O_7$.", Phys. Rev. B **38**, 7160 (1988).

2) S.J. Hagen, Z.Z. Wang and N.P. Ong, "Anomalous paraconductivity in single crystal $YBa_2Cu_3O_7$.", Phys. Rev. B **38**, 7137 (1988).

3) J. Clayhold, N.P. Ong, P.H. Hor, and C.W. Chu, "Hall effect of the high-T_c superconducting oxides Bi-Ca-Sr-Cu-O and $Tl_2Ca_2Ba_2Cu_3O_x$.", Phys. Rev. B **38**, 7016 (1988).

4) J. Clayhold, S. Hagen, Z.Z. Wang, N.P. Ong, J.M. Tarascon and P. Barboux, "Chain-site vs. plane-site Cu substitution in $YBa_2Cu_{3-x}M_xO_7$ (M=Co,Ni): Hall and thermopower studies.", Phys. Rev. B **39**, 777 (1989).

5) X.D. Shi, R.C. Yu, Z.Z. Wang, N.P. Ong and P.M. Chaikin, "Sound velocity and attenuation in single-crystal $YBa_2Cu_3O_{7-\delta}$.", Phys. Rev. B **39**, 827 (1989).

6) J. Clayhold, N.P. Ong, Z.Z. Wang, J.M. Tarascon, and P. Barboux, "Hall effect anomaly in high-T_c copper-based perovskites." Phys. Rev. B **39**, 7324 (1989).

7) J. Clayhold, S.J. Hagen, N.P. Ong, J.M. Tarascon, and P. Barboux, "Approaching the Mott-Hubbard insulator in $Bi_2(Sr,Ca)_3Cu_2O_{8+d}$ by doping with Tm.", Phys. Rev. B **39**, 7320 (1989).

8) Z. Z. Wang, N.P. Ong, and J. McGinn, "Observation of large untwinned domains in single-crystal $YBa_2Cu_3O_7$.", J. Appl. Phys. **65**, 2794 (1989).

9) T.W. Jing, Z.Z. Wang, and N.P. Ong, "Gold contacts on superconducting crystals of $YBa_2Cu_3O_7$ with very low contact resistivity." Appl. Phys. Lett. **55**, 1912 (1989).

10) Yukio Watanabe, Z.Z. Wang, S.A. Lyon, D.C. Tsui, N.P. Ong, J.M. Tarascon and P. Barboux, "Mid-infrared reflectivity and ellipsometry measurements on single-crystal $YBa_2Cu_3O_7$ and $Bi_2Sr_2CuO_{6+y}$" Phys. Rev. B **40**, 6884 (1989).

11) S.J. Hagen, Z.Z. Wang, and N.P. Ong, "Anisotropy of the thermal conductivity of single crystal $YBa_2Cu_3O_7$", Phys. Rev. B **40**, 9389 (1989).

The following are review chapters in books or conference proceedings.

12) N.P. Ong, T.W. Jing, Z.Z. Wang, J. Clayhold, S. Hagen, and J.M. Tarascon, "Electronic properties of $YBa_2Cu_3O_7$ in the normal and superconducting states." *High temperature superconductivity and other related topics*, edited by B.E. Baaquie et al. (World Scientific, Singapore 1989), p. 179.

13) T.R. Chien, Z.Z. Wang and N.P. Ong, "Discontinuous jump in transverse magnetization

of the flux lattice in $YBa_2Cu_3O_7$ crystals observed by torque magnetometry.", Physica C **162-164**, 343 (1989).

14) Z.Z. Wang, D.A. Brawner, T.R. Chien, N.P. Ong, J.M. Tarascon and E. Wang, "Temperature dependent Hall effect in $Nd_{2-x}Ce_xCuO_4$ and "60 K" $YBa_2Cu_3O_7$ single crystals." Physica C **162-164**, 1013 (1989).

15) T.W. Jing, Z.Z. Wang and N.P. Ong, "Andreev reflection and the proximity effect in Au-$YBa_2Cu_3O_7$ junctions with ultra-low interface resistance.", Physica C **162-164**, 1061 (1989).

16) T.W. Jing, Z.Z. Wang, N.P. Ong, J.M. Tarascon and E. Wang, "Andreèv reflection and tunneling results on $YBa_2Cu_3O_7$ and $Nd_{2-x}Ce_xCuO_{4-y}$ single crystals." in *Superconductivity and Applications*, edited by H.S. Kwok, Y.H. Kao, and D.T. Shaw (Plenum 1990), p. 323.

17) N.P. Ong, T.W. Jing, Z.Z. Wang, J. Clayhold, S.J. Hagen, and T.R. Chien, " Andreèv Reflection, thermal conductivity, torque magnetometry, and Hall effect in the high T_c systems." to appear in *Strong Correlations and Superconductivity,* edited by H. Fukuyama, S. Maekawa, and A.P. Malozemoff, Springer Ser. Sol. State Sci. **89** (Springer, 1989), p. 204.

18) N.P. Ong, "The Hall Effect and Its Relation to Other Transport Phenomena in the Normal State of the High-Temperature Superconductors.", in *Physical Properties of the High-Temperature Superconductors, vol. 2,* edited by D.M. Ginsberg (World Scientific, Singapore 1990), 459.

Graduate students fully supported

i) Jeff Clayhold (awarded PhD in June 1989).
ii) Steven Hagen (awarded PhD in June 1989).

Postdoctorals supported (partially)

i) Tian Wei Jing (30%)
ii) Zhao Zhong Wang (30%).

Description of work accomplished

The abbreviations used for the various oxides are "*123*" (for $YBa_2Cu_3O_7$), "*214*" (for La_2CuO_4), "*Bi 2212*" (for $Bi_2Sr_2CaCu_2O_8$), "*Tl 2212*" (for $Tl_2Ba_2CaCu_2O_8$) and "*Tl 2223*" (for $Tl_2Ba_2Ca_2Cu_3O_{10}$).

1) Anisotropic thermopower of single-crystal *123*

We have measured the out-of-plane thermopower S_c and the in-plane thermopower S_{ab} in single crystals of thickness exceeding 100 μm. As expected from previous work on the anisotropic electrical resistivity, we found that S_{ab} is qualitatively distinct from S_c, especially in their T-dependence. S_c is always positive and increases with increasing T (approx. as $aT + bT^2$). It attains ~10 μV/K near 300 K. However, S_{ab} is weakly T-dependent (and of the order of 2-4 μV/K). Its sign may be positive or negative. (Paper 1 of listing in previous page.)

2) Anomalous paraconductivity of single crystal *123*

Whereas several reports had been published on the paraconductivity in *123* these were mostly on sintered samples or polycrystalline films. We showed that in single crystals the in-plane paraconductivity s' is strictly two-dimensional for T varying from 1 K to 200 K above T_c, i.e. $\sigma' \sim t^{-1}$ where $t = (T-T_0)/T_c$ is the reduced temperature. Instead of a slow crossover from a 2D to 3D behavior, we find that σ' undergoes an abrupt jump at a temperature 0.5 K above the observed T_c. (See **Fig. 1**).The jump is especially abrupt in crystals with very narrow transitions ($\Delta T < 0.1$ K). We showed that the Lawrence-Doniach model is incapable of describing the sharp jump from 2D to 3D behavior which occurs 0.5 K above T_c. No evidence for the Maki-Thompson term is obtained. (Paper 2).

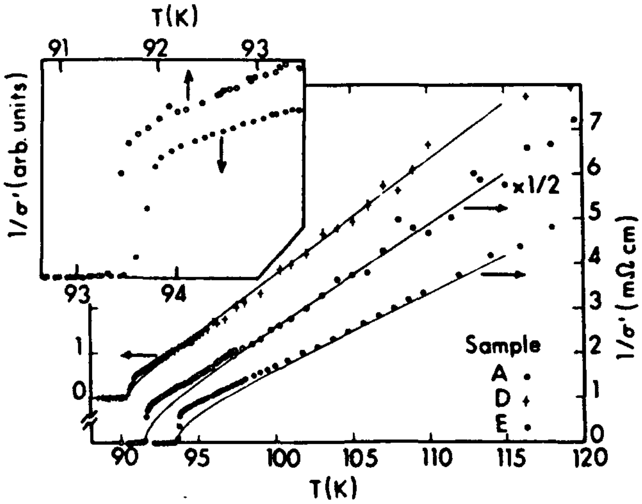

FIG 1 (Main panel) Plot of the reciprocal of the paraconductivity versus temperature in three single crystals of *123*. The solid lines are the anisotropic effective-mass model of Lawrence and Doniach. The jump to zero resistance is much sharper than predicted by the effective mass model. The inset shows the behavior near T_c. (From Hagen, Wang and Ong, paper 2)

3) Hall and thermopower of sintered *123* doped with Ni and Co

Many groups have studied the suppression of T_c in *123* when Cu is substituted with the 3d series of transition metals as well as Zn, and Al. Most studies concur that whereas Zn and Ni enter the plane sites (Cu2), Co and Al enter the Cu1 sites. By thermopower, resistivity and Hall studies on Ni and Co doped sintered 123, we have found a distinct difference between in-plane and chain substitution. The former (Ni) does not alter the carrier concentration as probed by R_H, but, nevertheless, suppresses T_c rapidly. We have interpreted this as a disorder effect strongly affecting the coherence of the electronic state responsible for high-T_c behavior. This is distinct from the effect of decreasing the carrier concentration n. Co doping, on the other hand, strongly depletes the carrier density in the CuO_2 planes. (n decreases exponentially as the Co concentration x increases.) We argue that the carrier depletion does not come from the trivalency of Co (which is cancelled by the extra oxygen bound to the Cu1 site). Neutron studies show that the bridging oxygen O4 is increasingly pulled towards the Cu1 with increasing x. This changes the chemical potential of the planes relative to the chains, thereby transferring electrons into the planes from the chains. (Paper 4).

4) Temperature dependence of the Hall coefficient in high-T_c oxides

From our Hall studies on the *214, 123, Bi 2212* and *Tl 2223* systems, we have deduced a common pattern in the T-dependence of R_H and a suggestive correlation between the slope dn_H/dT and T_c in each of these four families. In all these compounds dn_H/dT is always positive, with *123* showing the strongest T-variation. When T_c is suppressd (for e.g. in Co doped *123*) the slope dn_H/dT is also systematically suppressed (**Fig. 2**). This slope suppression is observed in Co and Pr doped *123*, oxygen doped *123*, Ni doped *214*, and Tm doped *Bi 2212*. The T-dependence of R_H is unlikely to be due to a particular combination of electron and hole bands, since it is so pervasive. Also, doping with Co and Pr in *123* show conclusively that such fortuitous band cancellations cannot be correct. We propose that the T-dependence is a generic property (leading to a skew scattering) of the electronic state peculiar to high T_c compounds and whenever, T_c is suppressed by doping, this characteristic T-dependence is also suppressed. (Paper 6).

5) Approaching the metal-insulator transition in *Bi 2212* doped with Tm

Tarascon et al have shown that when Bi *2212* is doped with Tm or any of the trivalent rare earths Er, Y, Ho the resistivity increases rapidly for x > 1.4 (in the stoichiometry $Bi_4Sr_3Ca_{3-x}Tm_xCu_4O_{16+y}$). We measured the variation of the Hall coefficient R_H versus both T and x in a range of samples and found that n_H (= $1/R_H$) decreases linearly with increasing x, extrapolating to zero at x = 1.4. (ρ undergoes a rapid increase of 100 in this range.) We interpret

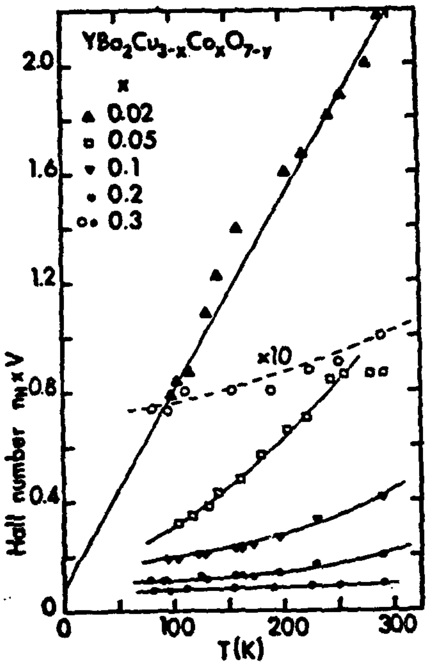

FIG 2 Variation of the Hall coefficient R_H with temperature in ceramic samples of *123* doped with Co. The Co content x is indicated for each sample. In the x=0 sample, the Hall number $n_H = 1/(eR_H)$ is linear in T. As x increases, the slope dn_H/dT is suppressed. Simultaneously, there is a rapid decrease in the overall magnitude of n_H. (From Clayhold, Ong, Wang, Tarascon, and Barboux, paper 6).

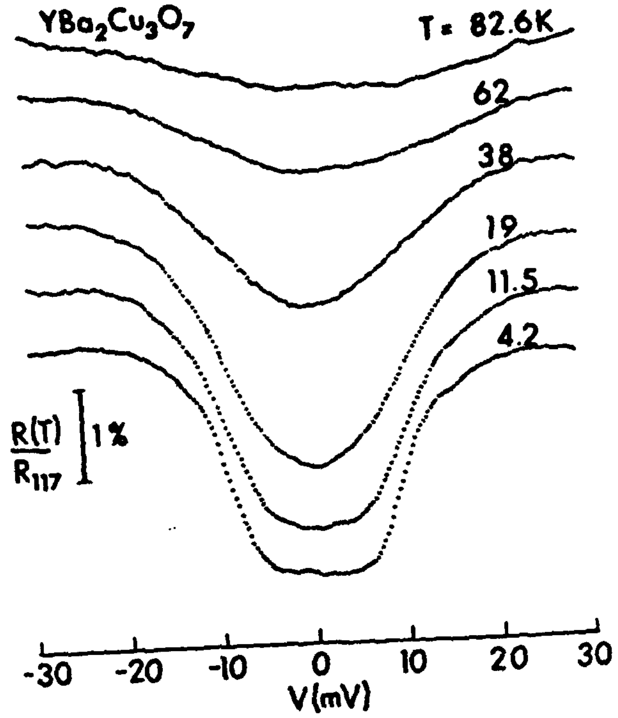

FIG 4 The in-plane thermal conductivity vs. temperature in three *123* crystals. In all samples, κ_{ab} equals ~ 8 W/Km at 100 K, or about twice the electronic contribution calculated from the Wiedemann-Franz law (using the measured in-plane resistivity). In one sample (triangles) there is a slight increase in κ_{ab} as T increases towards 300 K. The large anomaly below T_c is also observed in ceramic samples, but is absent in the out-of-plane direction. (From Hagen, Wang and Ong, paper 11.)

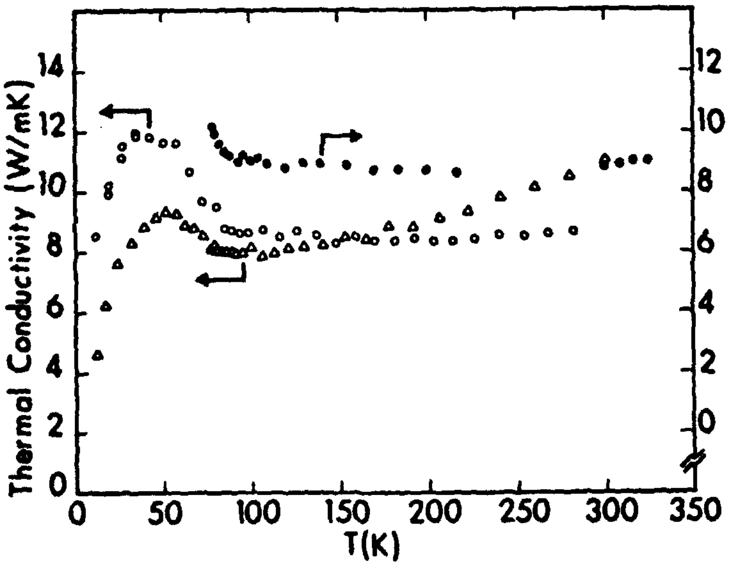

FIG 3 The *R vs. V* curve for a (Type B) Au-*123* junction measured with a Au point contact touching the Au film. R = *dV/dI* is normalized to the curve at 117 K. As *T* decreases below 60 K, a distinct gap opens up in the *R-V* curve. We interpret this gap as due to the Andreev reflection of injected electrons at the Au-*123* interface. The magnitude of the gap is ~10 mV. (From Jing, Ong, Wang and Anderson, paper 9).

this behavior as consistent with a Mott Hubbard model in which the chemical potential μ is near the middle of the lower Hubbard band at x = 0. μ is pushed into the Hubbard gap when x increases to 1.4. This behavior is directly in conflict with band structure calculations. From the Hall data we also found that the carrier density (at x = 0) is close to 0.42 holes per Cu ion. (Paper 8).

6) Andreev reflection studies in single crystal *123*.

Following a paper by Hoevers et al reporting the observation of Andreev reflection from polycrystalline *123* film at 1.2 K, we started a systematic program to investigate this important effect. We have explored the junction formed between Au and single crystal *123* using various fabrication techniques. In Type A junctions we sputter etch a crystal, expose it to air for a few minutes, then sputter on a Au film 1000 Å thick. A junction impedance of ~0.5 Ω is obtained. Strong Andreev reflection was consistently observed in these junctions. However, the gap Δ is only 1-3 mV at 4.2 K, and vanishes close to 60 K. We identify Δ with the damaged surface of the crystal which is either in the "60 K" phase or becomes superconducting by proximity with an underlying "60K" phase. Much larger gaps are seen in Type B junctions with sharper interfaces. In Type B junctions we first cleave the crystal in high vacuum and then evaporate a thin Au film (<200 Å) without cracking the vacuum. This leads to very low impedance junctions (< 10 μΩ, or a specific contact resistivity of under 10^{-9} Ω cm^2). Tunneling studies into these new junctions using a point contact shows a distinct gap structure of magnitude Δ = 10 mV (**Fig. 3**). (Paper 9).

7) Thermal conductivity of single-crystal *123*

We have measured the thermal conductivity anisotropy of single crystals of *123* and obtained the following conclusions. The in-plane component κ_{ab} is twice as large as obtained in ceramics above T_c, and is almost T-independent in two samples. In a third, κ_{ab} shows a weak tendency to increase with T (See **Fig. 4**). Using the Wiedemann-Franz law, we find that electronic component accounts for 50% of the measured κ_{ab}. The remainder is likely due to phonons which are strongly scattered by the carriers. Below T_c, κ_{ab} shows a prominent maximum, peaking at 50 K. For the out-of-plane direction, κ_c vs. T is quite typical of insulating crystals. It shows a weak maximum below 40 K and decreases slowly with increasing T at high temperatures. We argue that the lattice conduction is responsible for the peak in κ_{ab} below T_c, implying that the electron-phonon coupling is significant in-plane. On the other hand, the absence of any anomaly or break-in-slope in κ_c at T_c shows that the electron-phonon coupling is almost 40 times weaker. (Paper 11).

8) Magnetization anisotropy of single crystal by torsional magnetometry

An important quantity to determine is the anisotropy γ of the coherence lengths ξ_{ab}/ξ_c (in-plane/out-of-plane). Although this can be deduced from H_{c2} measured by magnetoresistance, these measurements are not without uncertainties because of flux flow. We have built a torsion magnetometer operating in a field H up to 1 T. By orienting **H** at an angle θ to the **c** axis, we can measure the torque acting on *123* crystals due to the anisotropy of the diamagnetic moment (See **Fig. 10**). Farrell et al previously used this method on aligned ceramics to deduce a value for γ of 5 at 77 K. In our single crystals we have derived a value for γ equal to 5.8 ± 0.3. Unlike the ceramic data, we find hysteretic behavior in τ vs. θ plot even for temperatures 0.5 K below T_c. (Paper 12).

9) Domain structure of single crystal *123*

By examining a large number of single crystals of *123* with both polarized light microscopy and transmission electron microscopy we have found that about 10% of the crystals have very large domains (> 100 x 100 μm^2 is area) which are untwinned, yet orthorhombic. We demonstrated that these were orthorhombic from the diffraction spots. The twinning structure was also studied in detail in the region where the minority domain running in one direction meets up with domains running in the orthorgonal direction. (Paper 7)

10) Mid-infrared reflectivity and ellipsometry measurements of single-crystal *123* and *Bi 2201*.

The reflectivity R of single crystals of *123* has been measured in the range 600 cm^{-1} to 9,000 cm^{-1} using near-normal incidence reflection and also at 48^{o} incidence reflectivity in both the transverse magnetic and transverse electric modes. By careful attention to instrumental stability and sample quality we managed to obtain a reflectivity which has a maximum variance of 4 % over the whole mid IR range. R is consistently higher than in all previous reports for *123*. We fit R to a simple Drude-Lorentz model and find the effective mass of carriers to be $2m_0$ (m_0 = free electron mass). The carrier scattering rate $1/\tau$ is found to be 3.1 k_BT/h at room temperature. We discuss the validity of this model and the existence of a broad and flat absorption band between 4,000 and 9,000 cm^{-1}. We compare our results with those of other groups. (Paper 10).