Transport and magnetic properties of $Tl_2Ba_2CuO_{6+\delta}$ showing a δ-dependent gradual transition from an 85-K superconductor to a nonsuperconducting metal

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(Received 13 August 1990)

Transport and magnetic properties are investigated for $Tl_2Ba_2CuO_{6+\delta}$, which shows a gradual transition from an 85-K superconductor to a nonsuperconducting normal metal, as the excess oxygen content δ is increased from ~ 0 to ~ 0.1. Hall measurements demonstrate that this transition arises from an overdoping of the hole carriers by excess oxygen. The temperature dependence of the resistivity is well fitted to a power-law dependence for all δ's, while the exponent shows a systematic change from linear ($\delta \sim 0$) to quadratic ($\delta \sim 0.1$) dependence. No significant changes of the Hall coefficient nor spin susceptibility are observed at the superconductor-metal phase boundary, suggesting a similarity and continuity between both the electronic structures. This is in sharp contrast to the previous observations for $La_{2-x}Sr_xCuO_4$.

I. INTRODUCTION

At the first stage of the study of thallium system superconductors, it was quite mysterious why the T_c values varied so much from sample to sample in spite of their apparently identical crystal structures. We first pointed out that the T_c variations were caused by a change in oxygen content as small as 0.1 per formula unit.[1-3] In a series of compounds with ideal composition $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, variations in T_c are 0–85 K, 85–110 K, and 116–110 K for $n=1$, 2, and 3, respectively.[3] It is noted that these three phases commonly have double TlO layers in their crystal structures, whereas little variations in T_c were found for TlO single layer compounds.

Very recently, we carried out neutron diffraction measurements on the $n=1$ compounds with various T_c values and revealed that oxygen atoms are incorporated and released at an interstitial site between the double TlO layers.[4] This is really the reason why T_c variations are observed only for TlO double layer compounds, not for TlO single layer compounds. Thus, these TlO double layer compounds should be expressed as $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ ($n=1,2,3$; $\delta \sim 0$–0.1).

Among these compounds, the $n=1$ compound (Tl 2:2:0:1), having a single Cu-O octahedron layer, is the most interesting because it continuously changes from an 85-K superconductor to a nonsuperconducting normal metal as the excess oxygen content δ increases from ~ 0 to ~ 0.1. Hall measurements clearly demonstrate that the hole carriers are doped by the excess oxygen.[2] This strongly supports the idea that superconductivity is suppressed if the carrier concentration exceeds an optimum value, which was first pointed out by Torrence *et al.* for $La_{2-x}Sr_xCuO_4$.[5] Another example is $TlLa_{1-x}Ba_{1+x}CuO_5$ in which we have found an insulator–superconductor–normal metal transition with increasing x.[6] It should be noted that these three systems commonly have Cu-O octahedron layers in their crystal structures.

Until now, most studies have focused on an insulator-to-superconductor transition which takes place at a lower carrier density region than an optimum value. This is probably due to the fact that samples with lower carrier density have been easily available for most systems. On the contrary, a superconductor-to-normal metal transition has been observed only in a few systems as mentioned above. However, if we consider that superconductivity appears in an intermediate region between an antiferromagnetic insulator and a normal metal, or in other words, between spin liquid description and Fermi-liquid description, an investigating approach from a metallic side should be as important as that from an insulating side. The Tl 2:2:0:1 compound is the most suitable prototype for the study of the metallic side, because its T_c can be easily controlled in a wide range from 0 to 85 K by a simple annealing.

In particular, it is crucial to clarify whether any singularities exist at the superconductor–normal-metal phase boundary. Studies on $La_{2-x}Sr_xCuO_4$ have suggested some singularities in both Hall coefficient[7] and spin susceptibility,[8] that is, the Hall coefficient changes its sign from positive to negative and the spin susceptibility shows a maximum at the phase boundary. In the present study on the Tl 2:2:0:1 compound, however, we observe only gradual changes in both Hall coefficient and spin susceptibility at the superconductor–normal-metal boundary, which suggests the very similarity and continuity between both the electronic structures. In this paper, we will report the details of transport and magnetic properties of polycrystalline Tl 2:2:0:1 samples with various T_c's from 0 K to over 80 K controlled by hole doping through excess oxygen.

II. EXPERIMENTAL

Single-phase Tl 2:2:0:1 polycrystalline samples were prepared by solid state reactions similiar to those described in Ref. 3. X-ray diffraction did not detect any im-

purity phases in any of the samples. A few of the samples were also determined to be single phase by neutron diffraction. Samples sintered in an oxygen atmosphere were metallic and showed no superconductivity down to 2 K because of the excess oxygen. They were then annealed in argon atmosphere at various temperatures a range of 300–590 °C for 5 h, resulting in weight loss and the appearance of superconductivity with various T_c's depending on the annealing temperature. An additional annealing in an oxygen atmosphere restored both T_c and sample weight, and confirmed the clear relationship between T_c and the oxygen content. Thus in the present study, the excess oxygen content δ was estimated from its T_c value using the nearly linear correlation between T_c and the change in oxygen content, which was confirmed in our previous study.[3]

Resistivity and Hall coefficient were measured by the van der Pauw method using a disk sample of about 10 mm diam $\times$ 0.5 mm thick under a magnetic field of up to 8 T. The sample density was about 88% of the theoretical value. All data were obtained using a particular single sample whose T_c was repeatedly varied by argon or oxygen annealing. This makes the relative experimental error due to sample dimensions negligible, though the absolute dimensional error may amount to $\sim$10%. Meissner effect and normal susceptibility were measured using a Quantum Design MPMS SQUID susceptometer under magnetic fields of 10 Oe and 1 T, respectively. Again, each measurement was done on a particular single sample changing its T_c repeatedly.

In the present study, we defined T_c as (i) the zero-resistivity temperature for resistivity measurement, or (ii) the onset temperature of diamagnetism for magnetization measurement. We confirmed for several samples that these two definitions coincide within a few degrees.

III. RESULTS AND DISCUSSION

A. Meissner effect

The Meissner effect was investigated in order to evaluate the homogeneity of superconductivity for samples with various T_c's, although they had been confirmed to be quite homogeneous in a crystallographical sense.[1,4] To avoid the harmful effect of an inhomogeneous magnetic field in the susceptometer, the superconducting solenoid was once warmed up above the transition temperature to clean up the residual vortices, and a short scan length of 3 cm was applied. The Meissner signal was measured under various fields between 10 and 100 Oe. The ratio of the Meissner signal of the perfect diamagnetism (the Meissner fraction) was increased with decreasing applied field and almost saturated below 30 Oe. Thus, we show the data measured at 10 Oe in Fig. 1. All data in Fig. 1 were obtained using the same sample whose T_c was repeatedly changed. The demagnetization effect was ignored because the estimated demagnetization factor was less than 0.1.

As shown in Fig. 1, the superconducting transitions are rather sharp for most samples except for a few with $T_c > 20$ K. The samples with $T_c > 20$ K also show considerable Meissner fractions of 30–50 %. These facts indicate that the superconductvity is bulklike and homogeneous at least for samples with $T_c > 20$ K. On the other hand, it is noted that the Meissner fraction increasingly diminishes with lowering T_c, especially for $T_c < 20$ K. Since the Meissner fraction is affected by pinning force,[9] we also measured the shielding effect at low temperatures. The shielding fraction measured at 3 K under the fields of 10–50 Oe was above 60% for samples with $T_c > 30$ K. Then it gradually decreased with lowering T_c, but it still kept a significant amount of $\sim$50% even for samples with $T_c \sim 10$ K. Therefore, the observed decrease in the Meissner fraction does not necessarily mean inhomogeneity of the superconductivity. Although we cannot finally exclude the possible inhomogeneity due to inhomogeneous distribution of excess oxygen, both sharp transition and large shielding effect strongly suggest that the transition temperature of the system is continuously changed while preserving considerable homogeneity and bulk nature of the superconductivity over a wide range of 85–0 K by hole doping through excess oxygen.

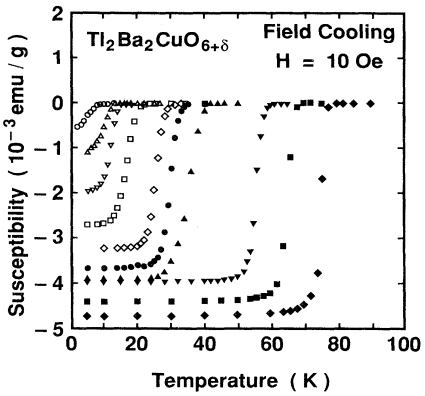

FIG. 1. Meissner signal measured under the constant field of 10 Oe for $Tl_2Ba_2CuO_{6+\delta}$ with various T_c's. All measurements were performed using the same sample whose T_c was repeatedly changed by annealing.

B. Resistivity

Temperature-dependent resistivities for samples with various T_c's are shown in Fig. 2. T_c and estimated δ values for each sample are listed in Table I. As δ increases, the normal resistivity decreases and its temperature dependence gradually deviates from the linear temperature dependence often observed for most high-T_c Cu oxides. To analyze those temperature dependences, we attempted fits of the data to a power-law temperature dependence expressed as

$$\rho = \rho_0 + AT^n . \quad (1)$$

The fitted results are demonstrated in Fig. 3 as a logarithmic plot of $(\rho - \rho_0)$ versus T, and the obtained values of ρ_0, n, and A are listed in Table I. As shown in Fig. 3, all data are well fitted to Eq. (1) over almost whole tempera-

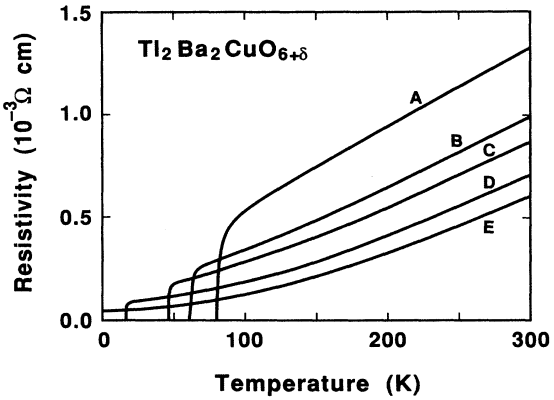

FIG. 2. Temperature dependence of the resistivity for $Tl_2Ba_2CuO_{6+\delta}$ with various T_c's. T_c and estimated δ values for each sample are listed in Table I. All measurements were performed using the same sample whose T_c was repeatedly changed by annealing.

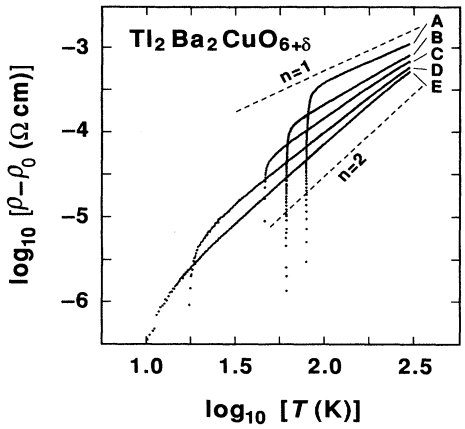

FIG. 3. Fit of the resistivity ρ in Fig. 2 to a power-law temperature dependence $\rho=\rho_0+AT^n$ shown on log-log scale. The dashed lines indicate the slopes for $n=1$ and $n=2$. Obtained values of ρ_0, n, and A are listed in Table I.

ture ranges of the measurement. In particular, the metallic nonsuperconducting sample (sample E) shows excellent fit in a wide temperature range at least from 20 K to over 200 K. It should be noted that such a power-law temperature dependence with $n\sim2$ over a wide temperature range is never interpreted in terms of the classical Bloch-Grüneisen (BG) theory based on electron-phonon interaction. In the BG theory, the exponent n is largely changed from ~1 to ~5 within a narrow temperature range of about one order of magnitude around the Debye temperature T_D. Roughly speaking, $n\sim1$ for $T>T_D$ and $n\sim5$ for $T<0.1T_D$. Therefore, the BG theory never explains the $n=2$ dependence over a temperature range of one order of magnitude. On the other hand, the linear temperature dependence ($n=1$) can be fitted to the BG formula if the Debye temperature is assumed to be small (<200 K).[10] However, considering the fact that the exponent n is gradually evolved from ~1 to ~2 with δ, the linear temperature dependence ($n=1$) should also be understood on the same basis as that for the quadratic temperature dependence ($n=2$), where the BG theory is found to be inapplicable. Recently, Tsuei[11] has indicated that both quadratic and linear temperature dependences are due to electron-electron scattering and that the linear term arises from a partial nesting of the two-dimensional Fermi surface. In addition, he implied a close relationship between high-T_c superconductivity and the Fermi surface nesting. Anyway, it is surely noteworthy that the transition temperature is clearly correlated with the temperature dependence of resistivity. High T_c (>80 K) is generally accompanied by a strong linear temperature dependence of resistivity. The present results reveal that excess hole doping gradually evolves the linear temperature dependence toward quadratic and lowers the transition temperature down to 0 K. And it is also noted that such gradual changes imply no singularity at the superconductor–normal-metal phase boundary.

C. Hall effect

The Hall coefficient R_H for samples with various T_c's is shown in Fig. 4(a). The Hall number n_H defined as $n_H=1/R_He$ and the Hall mobility μ_H are also shown in Figs. 4(b) and 4(c), respectively. Samples $A-E$ are corresponding to those of the resistivity data in Fig. 2, and their T_c's as well as the estimated δ's are listed in Table I.

TABLE I. T_c and estimated δ values for the $Tl_2Ba_2CuO_{6+\delta}$ samples used in the resistivity and Hall coefficient measurements. T_c was defined as the zero-resistivity temperature. δ was estimated from its T_c value using a nearly linear relationship reported in Ref. 3. The remaining columns list ρ_0, n, and A values obtained by the fit of resistivity data to a power-law temperature dependence expressed as $\rho=\rho_0+AT^n$.

Sample	T_c (K)	δ	ρ_0 (10^{-6} Ω cm)	n	A (10^{-8} Ω cm K^{-n})
A	81	0.01	130	0.95	505
B	62	0.03	125	1.26	65.3
C	47	0.05	120	1.49	15.9
D	16	0.08	82	1.67	4.47
E	0	0.10	51.5	1.88	1.27

As shown in Fig. 4(a), the Hall coefficient is positive and decreases with increasing excess oxygen content δ. This result clearly demonstrates the hole doping by the excess oxygen. For all samples, R_H shows a characteristic temperature dependence with a maximum at around 120 K. This feature is more clearly demonstrated by the temperature dependence of n_H as shown in Fig. 4(b), where n_H shows a minimum at around 120 K and linearly increases with temperature above 150 K. It is noted that each sample exhibits almost the same slope dn_H/dT. Therefore, we can express n_H as

$$n_H = n_0 + f(T) , \tag{2}$$

where $f(T)$ is such a function that has a minimum at around 120 K and linearly increases with temperature above 150 K. The present result means that the hole carriers doped by excess oxygen only increase the temperature-independent term n_0 and do not change the temperature-dependent term $f(T)$. This may suggest the existence of at least two kinds of hole carriers; one is the origin of $f(T)$ and probably related to the high-T_c superconductivity, and another has a T-independent character very similar to those in a normal metal. The hole doping by excess oxygen seems to increase the normal metallic component which would degrade the superconductivity. Figure 4(c) shows that the Hall mobility μ_H is increased by hole doping, indicating that the normal metallic component has higher mobility. Although at present we do not know the origin of the peculiar shape of $f(T)$, such a linear temperature dependence of n_H is quite popular in high-T_c Cu oxides. In particular, a very similar behavior of n_H with a minimum at $T > T_c$ is also observed for $La_{2-x}Sr_xCuO_4$.[12]

It should be emphasized that the Hall coefficient for Tl 2:2:0:1 does not show so much rapid decrease against the hole doping. This makes a sharp contrast to the results for $La_{2-x}Sr_xCuO_4$,[7] where the Hall coefficient rapidly diminishes with increasing x, and changes its sign from positive to negative as the system undergoes a

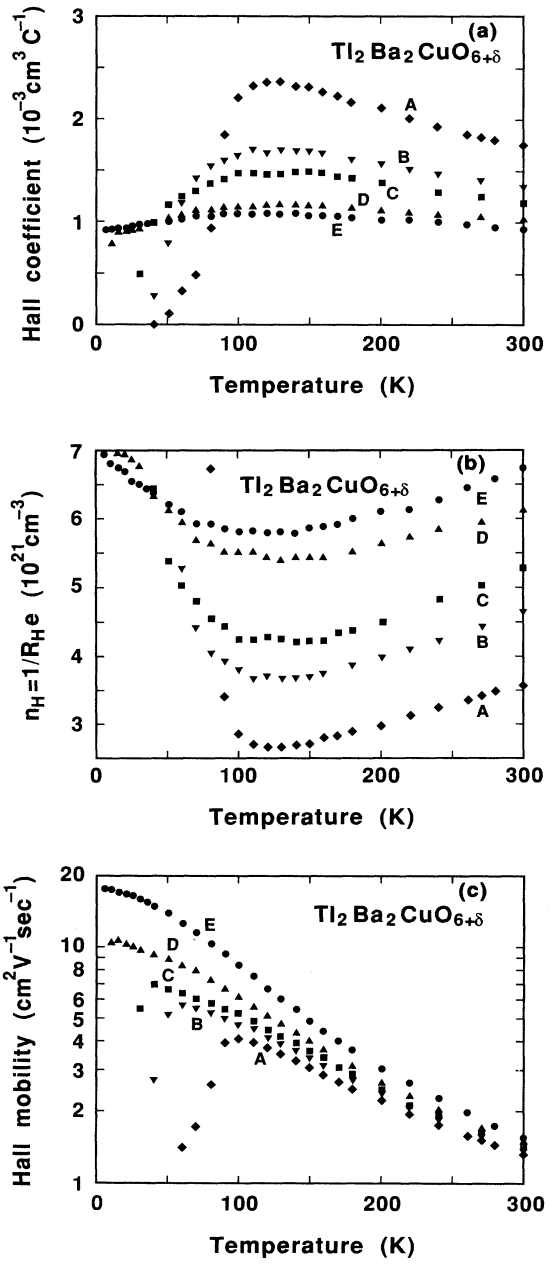

FIG. 4. Temperature dependences of (a) Hall coefficient, (b) Hall number, and (c) Hall mobility for $Tl_2Ba_2CuO_{6+\delta}$ with various T_c's. Data $A-E$ correspond to $A-E$ of resistivity data in Fig. 2, respectively. T_c and estimated δ values for each sample are listed in Table I. All measurements were performed using the same sample whose T_c was repeatedly changed by annealing.

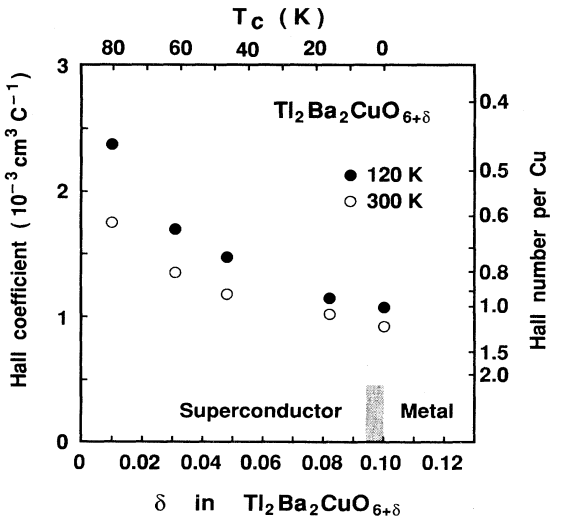

FIG. 5. Hall coefficient at 120 and 300 K plotted vs the excess oxygen content δ. The δ value was estimated from T_c which is shown on the upper scale. The right-hand scale shows the corresponding Hall number per Cu atom for convenience.

superconductor-to-nonsuperconducting metal transition. In Fig. 5, the Hall coefficients at 120 and 300 K are plotted versus the excess oxygen content δ. It is evident that the change in Hall coefficient is very gradual and suggests no singularity at the superconductor-metal phase boundary. Figure 6 shows the relationship between T_c and the Hall number per Cu atom at 120 K. T_c decrease from 81 to 0 K is accompanied with increase in the Hall number per Cu by 0.54. This value is three times larger than the expected value on the assumption that each excess oxygen creates two holes per Cu, because the corresponding increase in δ is about 0.09. Such a discrepancy, however, does not seem to be so anomalous in such a heavily doped metallic region, just as observed in $La_{2-x}Sr_xCuO_4$.[7] The important point to be noted is that the Hall number is not diverging but rather saturating with δ, showing gradual variation at the superconductor-metal phase boundary. This strongly suggests that the electronic structures of both phases are rather similar to each other.

We should discuss the problems arising from polycrystalline samples. We believe that the present results of transport properties on polycrystalline samples mainly reflect the in-plane properties because of the large electrical anisotropy. This situation was found to be appropriate for other high-T_c Cu oxides.[7] The present results show some indications such as T-linear resistivity and positive Hall coefficient with negative T dependence, which are, as a whole, very similar to the in-plane properties of $La_{2-x}Sr_xCuO_4$.[12] One essential difference is that R_H does not show rapid decrease even in a highly doped region. The question is whether this gradual change in R_H against the hole doping is an artifact of a polycrystalline sample. If the anisotropy is supposed to depend on the carrier concentration, we might observe a crossover from in-plane to out-of-plane properties, for example, a gradual δ dependence of R_H even though each component had a large δ dependence. Such compensation effects, however, would make the temperature dependence very complicated because each component should have a different temperature dependence. Therefore,

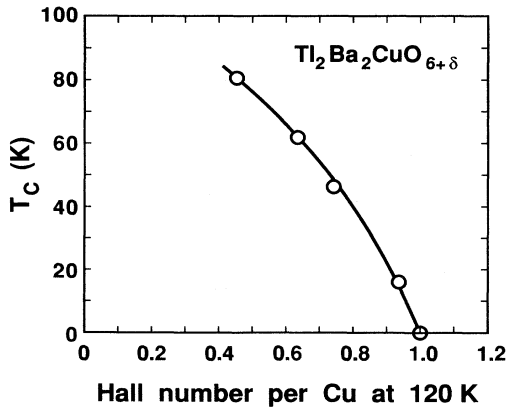

FIG. 6. Relationship between T_c and the Hall number per Cu at 120 K.

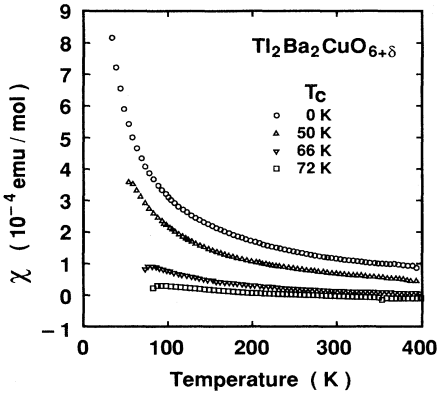

FIG. 7. Temperature dependence of the total measured magnetic susceptibility for $Tl_2Ba_2CuO_{6+\delta}$ with various T_c's. All measurements were performed at $H=1$ T using the same sample whose T_c was repeatedly changed by annealing.

considering the present results that the temperature dependence of n_H is almost unchanged by hole doping, the above supposition seems highly unlikely. Thus, the gradual δ dependence of R_H observed in a polycrystalline sample is considered to be intrinsic to the in-plane properties of the Tl 2:2:0:1 phase.

One important effect of a polycrystalline sample is an enhancement of both resistivity and R_H, which depends on the sample density. Although the density of the sample used in the present study is as high as 88% of a theoretical one, the observed values of resistivity and R_H may be somewhat larger than those for a single crystal. However, we should note that the sample density scarcely affects the overall behaviors including both T and δ dependences. We performed similar measurements on two other samples with densities of about 80% and 60%, and found that both resistivity and R_H showed the same δ dependences as those in the present results except for each multiplying factor.[2]

D. Magnetic susceptibility

The magnetic susceptibility χ shows a Curie-like upturn at low temperatures as shown in Fig. 7, although the Curie-like contribution becomes very small with increasing T_c (decreasing δ). All data can be approximately described by a simple Curie law of the form $\chi=\chi_0+C/T$. If we assume that the Curie term comes from Cu^{2+} with spin $\frac{1}{2}$ and $g=2.2$, the ratio of Cu^{2+} to Cu is estimated to be about 6% for the nonsuperconducting sample. In our previous paper,[13] we tentatively ascribed this Curie term to undetectable impurity phases such as $BaCuO_2$, because the magnitude of the Curie term depended on the sample preparation. However, it was recently found that even neutron diffraction measurements could not detect any impurity phases in our sample which showed a similar Curie-like behavior mentioned above.[4] This strongly signifies the difficulty in ascribing the Curie term as large as 6% to impurity phases. In addition, it seems more difficult to explain the considerable δ dependence of the

Curie constant in terms of impurities. To clarify this point, we synthesized $BaCuO_2$ which is probably an only magnetic impurity phase in the Tl-Ba-Cu-O system. The $BaCuO_2$ sample sintered in oxygen atmosphere showed a nearly Curie-Weiss-like behavior similar to those found in earlier studies.[14-16] However, following Ar reduction at 500 °C increased the Curie constant by about 40%. Although at present we do not know the reason why the Curie constant of $BaCuO_2$ is increased by reduction, this is apparently the opposite direction to that shown in Fig. 7. Thus, the Curie term cannot be ascribed to an impurity phase of $BaCuO_2$, but should be considered to be an intrinsic property of the Tl 2:2:0:1 phase.

For simplicity, we analyzed the total measured susceptibility χ using an expression

$$\chi=\chi_s+\chi_{\text{core}}+C/T\ , \tag{3}$$

where χ_s, χ_{core}, and C are Pauli spin paramagnetic susceptibility, temperature-independent core diamagnetic susceptibility (-1.93×10^{-4} emu/mol), and a Curie constant, respectively. Although we also attempted Curie-Weiss fit $C/(T-\Theta)$, the obtained paramagnetic Curie temperature Θ was at most 2 K, which scarcely affected the results above 100 K. Thus, we used a simple Curie law expression in Eq. (3). We subtracted the Curie term so as to minimize the temperature dependence of the residual part. The obtained χ_s data for samples with various T_c's are plotted versus temperature in Fig. 8. Although the subtraction procedure contains some uncertainty, we confirmed that it did not change the overall tendencies as shown in Fig. 8. That is, as δ increases (T_c decreases), χ_s increases and its temperature dependence gradually evolves from zero to slightly negative.

In the present analysis, we entirely excluded the Curie-like contribution from the spin susceptibility χ_s. However, considering that small Curie-like contributions are observed for $La_{2-x}Sr_xCuO_4$ with $x>0.2$,[7,8] it is not self-evident that χ_s does not show any Curie-like behavior. Very recently, Fujiwara *et al.*[17] have carried out the ^{63}Cu Knight shift measurement on our three samples with T_c's of 72, 40, and 0 K, and found that the Knight shifts in the normal state are quite temperature independent up to 100 K for all samples. Since the Knight shift is exclusively coupled to the spin suceptibility of conduction electrons, their results mean that the spin susceptibility does not contain any Curie-like contributions and that the Curie term in the bulk susceptibility is originated in some kinds of localized moments. Moreover, the spin part of the Knight shift, which is obtained by correcting the orbital shift and is proportional to χ_s, increases by a factor of about 1.5 with decreasing T_c from 72 to 0 K. This result shows an excellent agreement with the corresponding ratio of χ_s at 100 K in Fig. 8. Therefore, the obtained χ_s in Fig. 8 shows intrinsic features of spin susceptibility of the Tl 2:2:0:1 phase.

In Fig. 9, χ_s at 200 K and the Curie constant C are plotted versus the excess oxygen content δ. The present results are represented by open circles. It is noted that χ_s is linearly increased with hope doping. The Curie constant is nearly zero at $\delta\sim0$ while it is increased with δ and saturated at $\delta\sim0.05$. The saturated magnitude of the Curie constant corresponds to the Cu^{2+}/Cu ratio of about 6% as mentioned above. In Fig. 9, solid circles represent the data obtained in our previous study,[13] in which the Curie constants are shifted upwards while χ_s's downwards. We have measured more than ten samples with various Curie constants, and found that the increase in Curie constant was well correlated with the decrease in χ_s. This additional Curie constant can be ascribed to an impurity phase of $BaCuO_2$ which has a negative constant term of about -7×10^{-4} emu/mol besides a Curie-Weiss term. Since the previous data show the Curie constant of about 10%, the amount of $BaCuO_2$ is estimated at about 4%. Thus, χ_s should be corrected by 0.28×10^{-4}

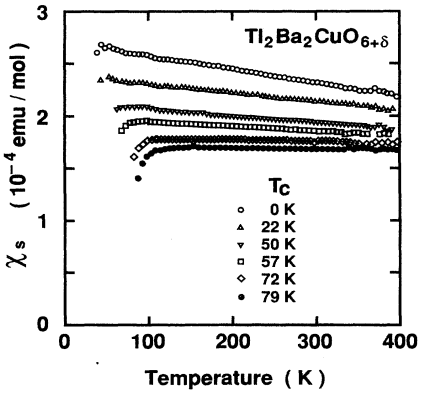

FIG. 8. Temperature dependence of the spin susceptibility χ_s for $Tl_2Ba_2CuO_{6+\delta}$ with various T_c's. χ_s was obtained by subtracting the Curie term and correcting the core diamagnetism as described in Eq. (3).

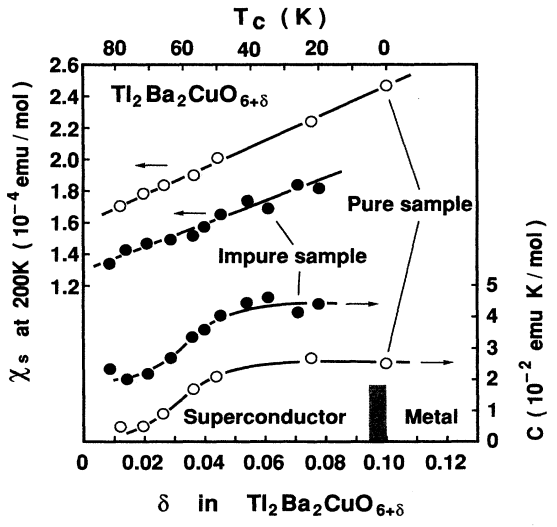

FIG. 9. Spin susceptibility χ_s at 200 K and the Curie constant plotted vs the excess oxygen content δ. The δ value was estimated from T_c which is shown on the upper scale. Open circles represent the present results on a pure sample, while solid circles represent the data in our previous study in which the sample seems to contain a small amount of $BaCuO_2$.

emu/mol, showing an excellent agreement with the present data.

Comparing the behaviors of χ_s with those for $La_{2-x}Sr_xCuO_4$,[7,8] some similarities are noted between them. In the La system, χ_s is also increased with decreasing T_c, showing very similar values (at 200 K) of $(1.7-1.9)\times10^{-4}$ and $(2.3-2.4)\times10^{-4}$ emu/mol for $T_c=40$ K (maximum) and $T_c=0$ K (metallic), respectively. However, it should be noted that χ_s for Tl 2:2:0:1 does not show any such singularities at the superconductor-metal phase boundary as observed in the La system, in which a maximum of $\chi_s(T)$ disappears and χ_s shows a maximum against the carrier concentration.[8] In Tl 2:2:0:1, χ_s shows a much smaller temperature dependence as shown in Fig. 8, which agrees well with the results of the Knight shift measurements.[17] And as shown in Fig. 9, χ_s is linearly increased with hole doping showing no maximum at the phase boundary.

Since χ_s is nearly temperature independent and monotonously increases with carrier concentration, the electronic structure may be close to that of a normal metal. If we assume that χ_s is connected to the Pauli paramagnetism expressed as $\chi_s=\mu_B^2N(E_F)$, the present results mean that the density of states at Fermi level $N(E_F)$ is linearly increased with carrier concentration. The calculated value of $N(E_F)$ using χ_s at 200 K changes from 5.0 states/eV f.u. ($\delta=0$) to 7.5 states/eV f.u. ($\delta=0.1$), which is somewhat larger than the band calculation result of 4.13 states/eV f.u.[18]

It is difficult to finally determine the origin of the intrinsic Curie term. It is noteworthy that the Curie term almost disappears at $\delta=0$, which strongly suggests the participation of excess oxygen. However, the nonlinear δ dependence of the Curie term indicates a complicated mechanism of appearance of local moments. Our speculation is that the Curie term arises from Cu^{2+} ions substituting for the Tl site. The substitution of Cu for Tl site is strongly indicated by the following facts:[4] (i) X-ray microanalysis always results in Tl-poor and Cu-rich compositions, typically Tl:Ba:Cu$=1.85-1.90:2:1.15-1.10$, (ii) a Cu-rich starting composition is necessary to obtain a pure sample, (iii) Rietveld analysis of x-ray diffraction data suggests that 3% of the Tl site is replaced by Cu. Considering the Tl^{3+} ionic radius of 0.95 Å, the Tl site should prefer Cu^+ (0.96 Å) rather than Cu^{2+} (0.72 Å). This is the situation for $\delta=0$, where the Cu^+ ion with no magnetic moment is substantially coordinated by two oxygen ions above and below. The excess oxygen atoms will intensify the structural modulation in TlO double layers and change the local oxygen coordination around Cu toward that of Cu^{2+}, such as a square or an octahedron, arising a local moment. In addition, it is also noted that the substitution of Cu for Tl site can explain the origin of hole carriers for samples with no excess oxygen.

IV. CONCLUSION

We have measured transport and magnetic properties of $Tl_2Ba_2CuO_{6+\delta}$ which shows a δ-dependent gradual transition from an 85-K superconductor to a nonsuperconducting normal metal. Hall measurement demonstrates that this transition is due to overdoping of hole carriers by excess oxygen. The Meissner and shielding measurements indicate that the transition temperature is continuously changed from 85 to 0 K without losing the bulk nature and homogeneity of the superconductivity.

Temperature dependence of the resistivity is well fitted to a power-law dependence for all T_c's, which is difficult to be explained in terms of electron-phonon scattering. It is noted that T_c is strongly correlated with temperature dependence of the resistivity. High-T_c samples ($\delta\sim0$) exhibit a linear T dependence which is usually observed in high-T_c Cu oxides, while excess hole doping gradually evolves the T dependence toward quadratic and lowers T_c down to 0 K.

Temperature dependence of R_H shows a maximum at around 120 K irrespective of T_c. It is interesting that the Hall number $n_H=1/R_He$ shows the same linear temperature dependence for all δ's except for a constant term which increases with δ. This may suggest that the hole carriers doped by excess oxygen have a normal metallic character. In addition, n_H is gradually increased with δ, showing no remarkable change at the superconductor-metal phase boundary.

The magnetic susceptibility in the normal state shows nearly temperature-independent behavior after subtracting the Curie term which seems to be due to Cu^{2+} ions substituting for the Tl site. The obtained nearly T-independent spin susceptibility χ_s shows an excellent agreement with the results of the Knight shift measurement.[17] It is noted that χ_s is linearly increased with δ, showing no indication of singularity at the superconductor-metal phase boundary.

In the present results, the most important point to be noted is that the evolution of the system induced by excess hole doping is quite gradual. The 85-K superconductivity is gradually connected to the normal metal phase without any indication of discontinuity in both transport and magnetic properties, suggesting the very similarity and continuity between both the electronic structures. This might imply that the electronic structures of high-T_c materials are basically described as a Fermi liquid. It is noted that the present results show a sharp contrast with the previous observation for $La_{2-x}Sr_xCuO_4$,[7,8] where remarkable changes were observed at the superconductor-metal phase boundary. This difference might be related to the difference in the hole-doping mechanism. In Tl 2:2:0:1, holes are doped without disturbing the Cu-O octahedron layer because excess oxygen is incorporated in the TlO double layer. In the La system, however, holes are doped by Sr substitution for La, making the Cu-O octahedron layer essentially a solid solution.

Note added in proof. We have recently measured the in-plane resistivity and Hall coefficient of the Tl 2:2:0:1 single-crystal sample (metallic nonsuperconductor). The obtained results showed very good agreement with those for the polycrystal sample E in Figs. 2–4: the temperature dependence of the resistivity was quadratic and R_H was about $+1\times10^{-3}$ cm^3/C.

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