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# On the Determination of Hole Concentration in Thallium Cuprate Superconductors

A. MANTHIRAM, M. PARANTHAMAN, AND J. B. GOODENOUGH

*Center for Materials Science and Engineering, ETC 5.160,*
*The University of Texas at Austin, Austin, Texas 78712-1084*

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We comment on a recent report of a wet-chemical procedure for determining the hole concentration in thallium cuprate superconductors. That report failed to address (a) the oxidation of reduced thallium by the bromine liberated by the oxidized copper and (b) the variation with Tl concentration of the overlap of the Fermi energy by the Tl 6*s* band in the double-Tl-layer compounds © 1992 Academic Press, Inc.

The known copper-oxide superconductors all have intergrowth structures consisting of $CuO_2$ sheets alternating with other layers along the *c*-axis. Oxidation/reduction of the $CuO_2^{2-}$ sheets above/below the formal Cu valence 2+ is one of the necessary conditions to suppress the long-range antiferromagnetic order and induce superconductivity. Muon spin relaxation experiments have shown (*1*) that $T_c$ varies in *p*-type superconductors with the mobile charge-carrier density *p* and its effective mass $m^*$ as

$$T_c \propto p/m^* \tag{1}$$

until it saturates at a higher $p/m^*$ value. Although the $T_c$ vs *p* relationship has been established for simple systems like $La_{2-y}Sr_yCuO_4$ (*2*), such a correlation was hindered for thallium cuprate superconductors—$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ and $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$—mainly because of the inability to know the thallium and oxygen contents in the material. Recently we showed (*3, 4*) that the thallium and oxygen contents can be determined without any ambiguity by simple wet-chemical procedures.

The thallium content is determined by a selective precipitation of Tl as a perchlorate–thiourea complex followed by filtering and dissolving the precipitate in HCl, oxidizing all $Tl^+$ to $Tl^{3+}$ with bromine, treating with excess KI, and titrating the liberated iodine with thiosulfate solution. During this iodometric titration all $Tl^{3+}$ is quantitatively reduced to $Tl^+$ according to the reaction

$$Tl^{3+} + 2I^- \rightarrow Tl^+ + I_2 \tag{2}$$

and from the titer value the total thallium content can be determined. The validity of this procedure was confirmed by carrying out the experiment under identical conditions with known quantities of either $Tl_2O_3$ or a mixture of $Tl_2O_3$ and $YBa_2Cu_3O_{6.94}$. The

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TABLE I

ANALYTICAL DATA OF THALLIUM CUPRATES

| Nominal composition | Tl content | Oxygen content | Oxidation state of Cu[a] | Hole concentration in the $CuO_2$ sheets | $T_c$ (K)[b] |
|---|---|---|---|---|---|
| $Tl_2Ba_2CuO_6$ | 1.82 | 5.49 | 1.52+ | — | 74 |
| $Tl_2Ba_2CaCu_2O_8$ | 1.79 | 7.59 | 1.90+ | — | 94 |
| $Tl_{2.1}Ba_2CaCu_2O_8$ | 1.90 | 7.63 | 1.78+ | — | 77 |
| $Tl_2Ba_2Ca_2Cu_3O_{10}$ | 1.67 | 9.41 | 1.94+ | — | 100 |
| $TlBaLaCuO_5$ | 0.83 | 4.75 | 2.01+ | 0.01 | Semiconducting |
| $TlBa_{1.4}La_{0.6}CuO_5$ | 0.87 | 4.71 | 2.21+ | 0.21 | 23 |

[a] Obtained by assuming all $Tl^{3+}$ in the solid. A value less than 2.00 in the superconducting sample indicates that there is an overlap of the Tl 6*s* band with the conduction band. In the case of "$TlBaLaCuO_5$" and "$TlBa_{1.4}La_{0.6}CuO_5$" the actual hole concentration is obtained without any difficulty since all Tl is present as $Tl^{3+}$.

[b] Diamagnetic onset temperature from ac susceptibility measurements.

procedure gave thallium contents with an error of ±1%.

The total oxygen content is determined by dissolving a known quantity of the thallium cuprate in 2 *N* HBr, treating the solution with excess KI, and titrating the liberated iodine with thiosulfate solution. During this iodometric titration all the oxidized thallium is quantitatively reduced to $Tl^+$ as

$$Tl^{(1+n)} + nI^- \rightarrow Tl^+ + \frac{n}{2}I_2 \quad (3)$$

and all the oxidized copper is quantitatively reduced to $Cu^+$ as

$$Cu^{(1+n)} + nI^- \rightarrow Cu^+ + \frac{n}{2}I_2; \quad (4)$$

therefore, from the titer value the total oxidation present in the system above the formal valences $Tl^+$, $Cu^+$, and $O^{2-}$ and hence the total oxygen content can be obtained without any ambiguity since we know the exact Tl content in the material.

In cases where we know all thallium is present as $Tl^{3+}$—for example, single-Tl-layer compounds $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ (*4*, *5*)—we can determine the hole concentration *p* in the $CuO_2$ sheets by our procedure without any problem. On the other hand, in cases where the $Tl^{3+/+}$ couple overlaps the $Cu^{3+/2+}$ couple—i.e., the Tl 6*s* band overlaps the Fermi energy $E_F$ of the $CuO_2$ sheets—it is not possible to know the individual oxidations (hole concentrations) present separately in the $CuO_2$ sheets and $Tl_2O_2$ layers. In fact, no wet-chemical method that involves the dissolution of the material can distinguish/separate the individual oxidations; where two or more redox couples such as $Tl^{3+/+}$ and $Cu^{3+/2+}$ are simultaneously present in the same solid, internal oxidation/reduction reactions can take place upon dissolution according to the equilibrium aqueous redox potentials. Therefore, one can obtain only the total oxidizing power and hence the total oxygen content and not the individual hole concentrations in the $CuO_2$ sheets and $Tl_2O_2$ layers by wet-chemical procedures. Whether it is possible to estimate the individual hole concentrations from physical measurements depends on the measurement and situation.

On the other hand, we (*3*, *4*) were able to establish from our wet-chemical procedures that (a) the Tl 6*s* band does not overlap $E_F$—i.e., all Tl is present as $Tl^{3+}$—in the single-Tl-layer compounds $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ and (b) the Tl 6*s* band does overlap $E_F$—i.e., Tl has an average valence of

<3+—in the double-Tl-layer compounds $Tl_{2-y}Ba_2Ca_{n-1}Cu_nO_{2n+4}$, the extent of overlap decreasing sensitively with increasing $y$ (Tl vacancies). Nevertheless, the actual concentration of holes in the $CuO_2$ sheets could not be determined where the Tl 6*s* band overlaps $E_F$.

Subsequently Gopalakrishnan *et al.* (*6*) claimed that they could determine the hole concentrations in the $CuO_2$ sheets by dissolving the thallium cuprates in a mixture of HBr and $CCl_4$, followed by extracting the liberated bromine into the $CCl_4$ layer and titrating against the thiosulfate solution after treating with KI. Based on this procedure and a determination by our method of the total Tl concentration, they agreed with us (*3, 4*) that the oxidation of the $CuO_2$ sheets in $Tl_2Ba_2CuO_6$ is due to an overlap of the Tl 6*s* band with the conduction band of the $CuO_2$ sheets, but attempted to show that in the $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ it is due to Tl vacancies. They appear to have come to their conclusions without realizing (a) a few fundamental problems with their procedure and (b) that the overlap of the Tl 6*s* band with the conduction band varies sensitively with the actual thallium content in the material (*4*). We address these issues in this paper.

Dissolution of the thallium cuprates in a mixture of $CCl_4$ and HBr liberates bromine according to the reactions

$$Cu^{(2+\eta)+} + \eta Br^- \rightarrow Cu^{2+} + \frac{\eta}{2}Br_2 \quad (5)$$

and

$$Tl^{(3-\delta)+} + \frac{\delta}{2}Br_2 \rightarrow Tl^{3+} + \delta Br^-, \quad (6)$$

In the presence of the strong oxidizing agent bromine, any reduced thallium is oxidized to $Tl^{3+}$ according to reaction (6). Therefore the net amount of liberated bromine will be $(\eta - \delta)/2$ even though the actual amount of bromine liberated by the holes in the $CuO_2$ sheets is $\eta/2$. We have confirmed this fact by carrying out the experiment with $YBa_2Cu_3O_{6.94}$ and a mixture of known quantities of $YBa_2Cu_3O_{6.94}$ and $Tl_2O$. Therefore the procedure of Gopalakrishnan *et al.* (*6*) can determine only the hole concentration in excess of $Tl^{3+}$ and $Cu^{2+}$ and not the actual hole concentration in the $CuO_2$ sheets as they claim.

In cases where we know all Tl is present as $Tl^{3+}$ in the solid—for example, in the single-Tl-layer compounds $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$—reaction (6) does not occur and so the hole concentration determined by their procedure will represent the true hole concentration in the $CuO_2$ sheets. However, in such cases the actual hole concentration can be obtained by our procedure (*3, 4*) without any problem since we know the oxygen content and all Tl is $Tl^{3+}$. Furthermore, the experimental error in the procedure of Gopalakrishnan *et al.* (*6*) will be much larger than that in our procedure since their method needs a careful and quantitative separation of bromine in the $CCl_4$ layer from the aqueous layer having $Cu^{2+}$ and $Tl^{3+}$.

We have demonstrated (*4*) that the overlap of the Tl 6*s* band with the conduction band varies sensitively with the Tl content in the material. In the double-Tl-layer compounds $Tl_{2-y}Ba_2Ca_{n-1}Cu_nO_{2n+4}$, the oxidation of the $CuO_2$ sheets is predominantly due to (a) an overlap of the Tl 6*s* band with the conduction band for a smaller $y \approx 0.0$ and (b) Tl vacancies for a larger $y \approx 0.5$. In the double-Tl-layer compounds, the origin of holes in the $CuO_2$ sheets depends upon the actual Tl content in the material, whereas there is no overlap of the Tl 6*s* band in the single-Tl-layer ($y = 1$) compounds $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$.

Gopalakrishnan *et al.* (*6*) have obtained by their synthetic procedure compositions of $Tl_{1.95}Ba_2CuO_{5.93}$ (2201), $Tl_{1.62}Ba_2CaCu_2O_{7.75}$ (2212), and $Tl_{1.25}Ba_2Ca_2Cu_3O_{9.09}$ (2223). Since the 2201 phase has a Tl content close to 2.0 with $y = 0.05$, the Tl 6*s* overlap is present to the maximum extent possible.

Therefore this material does not give any net amount of bromine liberated; i.e., any bromine liberated in reaction (5) is consumed in reaction (6). Gopalakrishnan *et al.* did not observe any hole concentration with their procedure and therefore concluded that this observation indicates a different doping mechanism with the holes in the $CuO_2$ sheets in this compound produced by an overlap of the Tl 6*s* band in agreement with our results (*3, 4*).

In the case of the 2212 phase they had a Tl content of 1.65 with $y = 0.35$. We have shown (*4*) that with such a Tl content the Tl 6*s* overlap is still present, but to a lesser extent than that in the $y = 0.00$ case. Therefore the amount of bromine consumed in reaction (6) is less than that in the 2201 case. Therefore a net amount $(\eta - \delta)/2$ of bromine is liberated after reaction (6), which leads to the hole concentration $p = 0.14$ reported by Gopalakrishnan *et al.* We would like to emphasize that the hole concentration reported by them in this case is not the actual hole concentration in the $CuO_2$ sheets. The actual hole concentration in the sheets will be larger than what they have reported because of the participation of reaction (6). It should be noted that if they had prepared the 2212 phase with a Tl content close to 2.0, then they should not have observed by their method any hole concentration at all as in the 2201 case. In fact, we prepared both $Tl_{1.9}Ba_2CaCu_2O_{7.63}$ (*4*) and $Tl_{1.79}Ba_2CaCu_2O_{7.59}$ and could deduce the presence of a Tl 6*s*-band overlap because the average copper valence of these *p*-type superconductors would be less than 2+ were all the thallium present as $Tl^{3+}$ (Table 1). Their method would have given zero hole concentration for these two samples because of reaction (6). Therefore one should not be misled into presuming that the origin of holes in the 2212 phase may be due only to Tl vacancies and not also to Tl 6*s*-band overlap in the 2212 phase.

In the case of the 2223 phase, they had a Tl content of 1.25 with $y = 0.75$. This Tl content is much below the stability limit $0.0 \leq y \leq 0.5$ for the double-Tl-layer compounds we have observed (*4*). Since it has $y = 0.25$, this composition may not have any Tl 6*s*-band overlap, in which case the hole concentration observed by them may be close to the actual hole concentration in the sheets. However, we prepared a $Tl_{1.67}Ba_2Ca_2Cu_3O_{9.41}$ sample that revealed the presence of Tl 6*s*-band overlap (Table 1).

In conclusion, the determination of actual hole concentration in the $CuO_2$ sheets is straightforward by our procedure (*3, 4*) in cases where there is no Tl 6*s* overlap, e.g., single-Tl-layer compounds $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. On the other hand, it is not possible by any wet-chemical procedure to determine the actual hole concentrations in the $CuO_2$ sheets in cases where the Tl 6*s* band overlaps the conduction band of the $CuO_2$ sheets as in the double-Tl-layer compounds $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$. However, we could demonstrate (*3, 4*) that the Tl 6*s* band overlaps $E_F$ in the double-thallium layer compounds and that the extent of Tl 6*s* overlap decreases sensitively with *y* to $y \approx 0.5$, where the Tl 6*s* overlap is minimal.

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