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Determination of Hole Concentration in Superconducting Thallium Cuprates*

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A chemical method for the determination of hole concentration in superconducting thallium cuprates is described. The method is based on selective oxidation of bromide ion by holes on CuO_2 sheets. Application of this method to several thallium cuprates has provided some insight into the origin of holes in these materials.

Most of the superconducting copper oxides known so far contain holes (arising from partial oxidation of CuO_2 sheets) as charge-carriers (*1*). The hole concentrations, n_h, per CuO_2 sheet is a vital parameter that characterizes the chemistry and physics of these materials including the superconducting transition temperature, T_c (*2, 3*). Chemical titrations using I^- or Fe(II) as reducing agent provide a convenient means of determining the n_h in La_2CuO_4 (214), $YBa_2Cu_3O_7$ (123), and bismuth cuprate superconductors (*4, 5*). A chemical method for the determination of hole concentration in thallium cuprates is, however, not available so far; methods using I^- or Fe(II) are not applicable to thallium cuprates because of interference from thallium(III). A chemical characterization of thallium cuprates reported recently by Manthiram *et al.* (*6*) does not enable a direct determination of hole concentration. Here we report a chemical titration method for the determination of hole concentration in thallium cuprates. The method is based on the finding that Br^- is selectively oxidized by holes on CuO_2 sheets and not by thallium(III). Using this method, we have determined the n_h values of a number of thallium cuprates including the series $TlBa_2Ca_{1-x}Y_xCu_2O_7$, where we find a definite T_c–n_h correlation similar to that found in other superconducting cuprates showing a maximum in T_c at an optimal hole concentration.

Our method makes use of HBr as the reducing agent which reacts selectively with the holes on copper liberating bromine. Tl(III) does not liberate bromine because under the experimental conditions employed, $TlBr_3$ is a stable compound. A method based on HBr has been used for the determination of n_h in the 214 and the 123 cuprates (*7*), but it cannot be employed as such for the case of thallium cuprates because selective titration of the liberated bro-

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mine in the presence of thallium(III) and copper(II) is not possible. We have overcome the problem by extracting the bromine into CCl_4. In what follows, we describe the titration procedure in detail.

A known quantity (~200 mg) of the sample covered with 25 ml of ice-cold CCl_4 in an Erlenmeyer flask is treated with 2 ml of 1 : 1 HBr. The sample dissolves when the contents are swirled for a couple of minutes, liberating bromine into the organic phase. Ice-cold distilled water (20 ml) is added at this stage to have a clear separation of the organic phase from the aqueous phase. The organic layer is then separated from the aqueous layer using a separating funnel. The aqueous layer is extracted with further aliquots of CCl_4 to remove all the bromine. The combined CCl_4 extracts containing all the liberated bromine are treated with 25 ml of ~0.5 *M* acidified KI. The iodine liberated is titrated with standardized 0.1 *M* sodium thiosulfate using starch as indicator. The formal Cu(III) content of the sample is obtained from the titer. The total copper and thallium contents of the sample are determined separately by using procedures reported already in the literature (*6*, *8*). The hole concentration, n_h, expressed as the ratio of the formal Cu(III) content to the total copper content, is then calculated. The validity of the method was checked by determining the hole concentration in standard samples and the n_h values agreed within ±0.006 (Table I).

We determined the n_h values of a number of thallium cuprates belonging to the single-thallium layer ($TlBa_2Ca_{n-1}Cu_nO_{2n+3}$) and double-thallium layer ($Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$) series prepared by (*9*, *10*) reacting the component oxides in sealed silver or silica tubes. When silica tubes were used, the samples were wrapped in platinum foils. Phase purity was checked by powder X-ray diffraction and only single-phase materials were used in the experiments. We also determined the total thallium content of each sample in order to characterize the chemical origin of the holes. Superconducting transition temperatures were determined by magnetic susceptibility and electrical resistivity measurements. The results are summarized in Table II.

TABLE I

DETERMINATION OF HOLE CONCENTRATION, n_h, IN CUPRATE SUPERCONDUCTORS BY THE METHOD DESCRIBED IN THIS PAPER USING HBr AND BY CONVENTIONAL METHODS USING I^-/Fe(II)

Compound	Hole concentration, n_h	
	HBr method	I^-/Fe(II) method
$La_{1.85}Sr_{0.15}CuO_4$	0.140	0.142
$YBa_2Cu_3O_{6.95}$	0.304	0.310
$YBa_2Cu_3O_{6.50}$	0.033	0.039
$Bi_2Sr_2CaCu_2O_{8+\delta}$	0.185	0.190

Determination of hole concentration of superconducting cuprate families has revealed the existence of a universal T_c–n_h correlation (*4*, *5*); plots of T_c vs n_h are generally dome-shaped curves showing a maximum in T_c at an optimal n_h. For example, the T_c–n_h plots of $La_{2-x}Sr_xCuO_4$ show a maximum T_c of 36 K for n_h = 0.15–0.24 (*2*). We considered it important to find out whether a similar T_c–n_h correlation existed in the thallium cuprates. We have chosen the $TlBa_2Ca_{1-x}Y_xCu_2O_7$ system which shows a superconductor–insulator transition as a function of composition [10, 11] for this purpose; $TlBa_2CaCu_2O_7$ is a superconductor with a T_c ~80 K, while $TlBa_2YCu_2O_7$ is an antiferromagnetic insulator (*12*). Our results (Fig. 1 and Table II) show that n_h decreases with increasing x in $TlBa_2Ca_{1-x}Y_xCu_2O_7$, indicating that holes are depleted, as expected, on replacing Ca by Y in the series. More importantly, a plot of T_c (R = 0) vs n_h for the series shows a dome-shaped curve with a broad maximum in T_c around 85 K occurring at n_h = 0.12–0.15 (Fig. 1). The results reveal that a T_c–n_h correlation

TABLE II

CHARACTERIZATION OF THALLIUM CUPRATES

Nominal composition	Synthesis conditions	Lattice parameters (Å) a	Lattice parameters (Å) c	Chemical analyses data: Thallium content	Chemical analyses data: Oxygen content	n_h	$T_c(K)^a$
$TlBa_2CaCu_2O_7$	890°C, 3 hr, sealed tube	3.842	12.66	0.70	6.21	0.163	80
$Tl_{0.9}Ba_2CaCu_2O_7$	890°C, 3 hr, sealed tube	3.848	12.75	0.59	6.06	0.170	73
$TlBa_2Ca_{0.75}Y_{0.25}Cu_2O_7$	890°C, 3 hr, sealed tube	3.850	12.65	0.63	6.22	0.148	86
$TlBa_2Ca_{0.7}Y_{0.3}Cu_2O_7$	890°C, 3 hr, sealed tube	3.852	12.63	0.74	6.38	0.119	82
$TlBa_2Ca_{0.5}Y_{0.5}Cu_2O_7$	890°C, 3 hr, sealed tube	3.858	12.58	0.66	6.33	0.084	62
$TlBa_2Ca_{0.4}Y_{0.6}Cu_2O_7$	890°C, 3 hr, sealed tube	3.864	12.56	0.72	6.45	0.063	16
$TlBa_2Ca_{0.25}Y_{0.75}Cu_2O_7$	890°C, 3 hr, sealed tube	3.870	12.54	0.73	6.50	0.033	—
$TlBa_2YCu_2O_7$	890°C, 3 hr, sealed tube	3.872	12.48	0.79	6.69	—	—
$Tl_2Ba_2CuO_6$	875°C, 3 hr, sealed tube, quenched	3.852	23.21	1.95	5.93	—	72
$Tl_2Ba_2CaCu_2O_8$	880°C, 3 hr, sealed tube	3.850	29.27	1.62	7.57	0.140	105
$Tl_{2.3}Ba_2CaCu_2O_8$	880°C, 3 hr, sealed tube, quenched	3.854	29.34	1.64	7.59	0.130	96
$Tl_2Ba_2Ca_2Cu_3O_{10}$	900°C, 1 hr, sealed tube, quenched	3.850	35.80	1.25	9.09	0.140	115

[a] T_c $(R = 0)$.

similar to that found in other cuprate superconductors exists for the single-thallium layer cuprates.

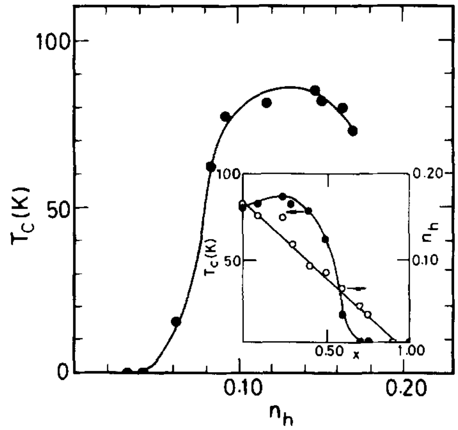

FIG. 1. The dependence of superconducting transition temperature (T_c) on hole concentration n_h, in the series $TlBa_2Ca_{1-x}Y_xCu_2O_7$. The variation of T_c and n_h with x for the same series of compounds are shown in the inset. Solid lines connecting the data points are guides to the eye.

Our results on double-thallium layer cuprates are equally interesting. Both the $n = 2$ and the $n = 3$ members of this family show an n_h value around 0.14, although the T_cs are different. Increasing the thallium content in the nominal $n = 2$ members during the synthesis yields materials with smaller n_h and correspondingly lower T_cs. Most surprisingly, the $n = 1$ member of the series does not show any holes at all ($n_h = 0$). We made several preparations of nominal $Tl_2Ba_2CuO_6$ which were single-phase materials with tetragonal structures exhibiting T_cs in the range 60–75 K. None of them showed a n_h by our titration procedure.

The absence of a chemically determinable hole concentration in superconducting $Tl_2Ba_2CuO_6$ may be taken to indicate that the origin of holes in this material is likely to be different from other thallium cuprates. Jung *et al.* (*13*) and Manthiram *et al.* (*6*) have suggested that an internal redox mechanism involving an overlap of the Tl : 6*s* band with the conduction band of CuO_2 gives rise to holes in the double-thallium layer cuprates. Among all the thallium cuprates investigated in this work and by Manthiram *et al.* (*6*), only $Tl_2Ba_2CuO_6$ is close to the ideal stoichiometric composition; all other materials are highly deficient in thallium and oxygen. It appears therefore that only in $Tl_2Ba_2CuO_6$ are holes created in the solid state by an internal redox mechanism

$$Tl^{III} + Cu^{II} \rightleftharpoons Tl^{III-\delta} + Cu^{II+\delta},$$

which involves an overlap of the Tl : 6*s* with the conduction band of the CuO_2 sheets. The holes created by this process are not detectable by the chemical titration described here. Holes in all the other thallium cuprates arise most likely from a thallium (and oxygen) deficiency. The possibility that holes arise from both effects in other double-thallium layer cuprates cannot be ruled out on the basis of chemical titrations. Determination of n_h by both Hall effect measurements and chemical titrations on the same samples may throw more light on this issue.

In summary, we have described a reliable chemical method for the determination of n_h in superconducting thallium cuprates. The method has enabled us to show the existence of a T_c–n_h correlation in single-thallium layer cuprates where the origin of the holes is mainly due to a thallium and oxygen deficiency. The correlation is similar to the one already known in other cuprate superconductors (*5*). In $Tl_2Ba_2CuO_6$ where there is no measurable n_h, the origin of the holes appears to be solely due to an internal redox process which involves an overlap of the Tl : 6*s* and the CuO_2 conduction band.

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References

1. See, for example, R. Beyers and T. M. Shaw *in* "Solid State Physics" (E. Ehrenreich and D. Turnbull, Eds.), Vol. 42, Academic Press, New York (1989).

2. J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, *Phys. Rev. Lett.***61**, 1127 (1988).

3. Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, *Phys. Rev. B* **38**, 7156 (1988).

4. M. W. Shafer and T. Penney, *Eur. J. Solid State Inorg. Chem.* **27**, 191 (1990).

5. C. N. R. Rao, J. Gopalakrishnan, A. K. Santra, and V. Manivannan, *Physica C* **174**, 11 (1991).

6. A. Manthiram, M. Paranthaman, and J. B. Goodenough, *Physica C* **171**, 135 (1990).

7. E. H. Appelman, L. R. Morss, A. M. Kini, U. Geiser, A. Umezawa, G. W. Crabtree, and K. D. Carlson, *Inorg. Chem.* **26**, 3237 (1987).

8. I. M. Kolthoff and R. Belcher "Volumetric Analysis-III", pp. 370–371, Interscience, New York (1957).

9. C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, *Science* **240**, 631 (1988).

10. A. K. Ganguli, R. Nagarajan, K. S. Nanjundaswamy, and C. N. R. Rao, *Mater. Res. Bull.* **24**, 103 (1989).

11. S. Nakajima, M. Kikuchi, Y. Syono, N. Kobayashi, and Y. Muto, *Physica C* **168**, 57 (1990).

12. J. Mizuki, Y. Kubo, T. Manako, Y. Shimakawa, H. Igarashi, J. M. Tranquada, Y. Fujii, L. Rebelsky, and G. Shirane, *Physica C* **156**, 781 (1988).

13. D. Jung, M.-H. Whangbo, N. Herron, and C. C. Torardi, *Physica C* **160**, 381 (1989).