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Chemical Bond Properties and Isomer Shifts of $Tl_2Ba_2Ca_2Cu_3O_{10}$

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$Tl_2Ba_2Ca_2Cu_3O_{10}$ was reported to be a superconductor with a highest transition temperature of 125 K among the homologous series of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$. The direct information on the Cu ion site at the atomic level is important for elucidating the superconductivity mechanism. The local bond properties of $Tl_2Ba_2Ca_2Cu_3O_{10}$ were studied using the average band-gap model. The calculated results show that the covalency of Cu(1)–O bond is 0.561, and the average covalency of Cu(2)–O is 0.296. Mössbauer isomer shifts of ^{57}Fe in $Tl_2Ba_2Ca_2Cu_3O_{10}$ were calculated using the chemical surrounding factor, defined by covalency and electronic polarizability. It is verified that for lower doping, Fe substitute the Cu at the Cu (1) site in forms of Fe^{3+} and Fe^{4+} ; for higher doping, Fe^{3+} and Fe^{4+} ion occupies Cu(1) and Cu(2) site respectively. The studies show that the determination of the correspondence between spectrum components and actual copper sites occupied by Mössbauer nucleus was made easier with the aid of the calculation results of the chemical bond parameters.

Key words: Superconductor, $Tl_2Ba_2Ca_2Cu_3O_{10}$, Chemical bond, Mössbauer effect

I. INTRODUCTION

$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1, 2, 3, 4$) are important high T_c oxide superconductor [1], which are orthorhombic, belonging to the D_{4n}^1 -P4/mmm space group with 2 formula unit per primitive cell [2]. The third member of the homologous series of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (Tl-2223) was reported to be a superconductor with a highest transition temperature of 125 K, which makes it the most attractive. The direct information on the Cu ion site at the atomic level is important for elucidating the superconductivity mechanism. So the need for a microscopic probe such as Mössbauer spectroscopy is self-evident. Mössbauer spectroscopy have been reported by Morrish [3]. However, the knowledge of the local environment of specific ions is still insufficient, because no theory can calculate the isomer shifts of complex compounds [4]. It has now been established both theoretically and experimentally that the concept of bond covalency is very important for explaining and classifying many basic properties in diverse areas including chemistry and condensed matter physics. Reviews concerning the bond covalency and its application had been made by Phillips, van Vechten (P-V) [5], and it has been accepted generally [6,7]. Further, this theory was successfully generalized to the multiple bond systems [8]. The important concept in the theory, such as covalency and polarizability etc, revealed the local information of the crystals. Therefore, P-V model may be reasonably employed to discuss Mössbauer isomer

shifts, which are strongly dependent on the local chemical environment of the Mössbauer nucleus [9-11]. In this work, $Tl_2Ba_2Ca_2Cu_3O_{10}$ has been investigated by considering all types of chemical bond. The chemical bond parameters and Mössbauer isomer shifts of Fe-doped in $Tl_2Ba_2Ca_2Cu_3O_{10}$ compound have been calculated. These results will contribute to a comprehensive understanding for high T_c superconductivity mechanism.

II. THEORY AND CALCULATION

According to their detailed structural data (see Fig.1), we can write the bond-valence equation as

$$\begin{aligned} Tl_2Ba_2Ca_2Cu_3O_{10} &= Tl_2Ba_2Ca_2Cu(1)Cu(2)_2O(1)_2O(2)_4O(3)_2O(4)_2 \\ &= \frac{1}{3}TlO(3) + \frac{5}{3}TlO(4) + \frac{8}{9}BaO(2)_{\frac{3}{2}} + \frac{8}{9}BaO(3)_{\frac{3}{2}} \\ &\quad + \frac{2}{9}BaO(4)_{\frac{3}{2}} + CaO(1)_{\frac{4}{3}} + CaO(2)_{\frac{4}{3}} \\ &\quad + Cu(1)O(1)_{\frac{3}{2}} + \frac{8}{5}Cu(2)O(2)_{\frac{5}{6}} + \frac{2}{5}Cu(2)O(3)_{\frac{5}{6}} \end{aligned}$$

For any binary crystal AB_n type compounds, consid-

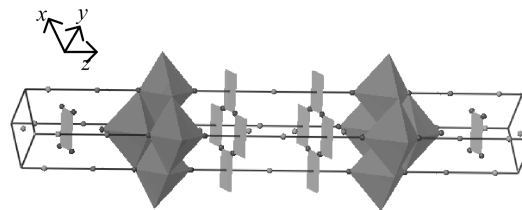


FIG. 1 Structure of $Tl_2Ba_2Ca_2Cu_3O_{10}$

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ering symmetry, let the middle point between A and B atom as the origin of coordinate. The Homilltonian is expressed as follows

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(\vec{r}) \quad (1)$$

Fourier expansion of the periodic potential, $V(\vec{r})$, is expressed as follows

$$V(\vec{r}) = \sum_G V_G \exp(i\vec{G} \cdot \vec{r}) \quad (2)$$

$$V_G = [V_A(\vec{G}) + V_B(\vec{G})]\cos(\vec{G} \cdot \vec{r}) + i[V_A(\vec{G}) - V_B(\vec{G})]\sin(\vec{G} \cdot \vec{r}) \quad (3)$$

Where, \vec{G} is reciprocal lattice vector; V_A and V_B is pseudopotential of A and B atom, the symmetric part, V_A+V_B , is called as homopolar potential V_c , and the antisymmetric part, V_A-V_B , is called as ionic potential V_i . Consequently, the average energy gap for every μ bond E_g^μ can be separated into homopolar E_h^μ and heteropolar C^μ parts

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (iC^\mu)^2 \quad (4)$$

The ionicity and covalence of any type of chemical bond is defined as follows

$$f_i^\mu = \left(\frac{C^\mu}{E_g^\mu}\right)^2, \quad f_c^\mu = \left(\frac{E_h^\mu}{E_g^\mu}\right)^2 \quad (5)$$

$$E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}} \quad (6)$$

$$C^\mu = \frac{14.4b^\mu e^{-k_s^\mu r_0^\mu}}{r_0^\mu} [(Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^*] \quad (7)$$

$$r_0^\mu = \frac{d^\mu}{2}, \quad k_s^\mu = \left(\frac{4k_F^\mu}{\pi a_B}\right)^{\frac{1}{2}} \quad (8)$$

$$(k_F^\mu)^3 = 3\pi^2 N_e^\mu \quad (9)$$

where a_B is the Bohr radius and n is the ratio of element B to element A in the subformula ($n>1$). ΔZ_A^μ is the correction factors of d electron [10]. $\Delta Z_A^\mu = M_A \times R_B$, where R_B is the anion radius, and M_A is fitted constant of A ion, its empirical value is 1.187 and 0.622 for Cu^{2+} (d^9) in square planar and pyramid site, respectively. k_F^μ is Fermi wave number of valence electron gas, N_e^μ is the numbers of valence electrons of type μ bond per cubic centimeter, b^μ is proportional to the square of the average coordination number N_c^μ

$$b^\mu = \beta(N_c^\mu)^2 \quad (10)$$

If the dielectric constant of the crystal is known, the value of β can be deduced by above equations. Kramers-Kronig relation of dielectric function at long wave limit

is written as

$$\begin{aligned} \varepsilon^\mu(\infty) &= 1 + \chi^\mu \\ &= 1 + \left(\frac{\hbar\Omega_p^\mu}{E_g^\mu}\right)^2 \left[1 - \frac{E_g^\mu}{4E_F^\mu} + \frac{(E_g^\mu)^2}{48(E_F^\mu)^2}\right] \end{aligned} \quad (11)$$

$$\varepsilon(\infty) - 1 = \chi = \sum_\mu F^\mu \chi^\mu \quad (12)$$

where, $\varepsilon^\mu(\infty)$ is dielectric constant of μ bond, χ is the macroscopic linear susceptibility, χ^μ is the total macroscopic susceptibility, E_F^μ is the Fermi energy, Ω_p^μ is the plasma frequency, F^μ is the fraction of bonds of type μ composing the actual complex crystal.

Using the β value (0.1172) of Y-123 superconductor [9], the chemical bond parameters of each type of chemical bond are calculated and listed in Table I. From which, it is find that the Tl-O, Ba-O and Ca-O types of bond possess higher ionic character and the Cu-O types of bond possess more covalent character. The Cu(1)-O possesses the highest covalency.

III. MÖSSBAUER ISOMER SHIFTS OF ^{57}Fe

It is well known within an oxidation state there is a spread in the isomer shift. This spread is governed by a number of factors related to the bond character, such as the coordination number, the covalency and the bond polarizability. By using these above elements, the chemical surrounding factor designated by the symbol h_e , has been proposed

$$h_e = \left(\sum_\mu \alpha_L^\mu f_c^\mu\right)^{\frac{1}{2}} \quad (13)$$

Where α_L^μ is the polarizability of the ligand bond volume in the μ bond. In recent work [10], it has been shown that linear relationships are observed between h_e and the isomer shift δ for a specific ion. The isomer shift for ^{57}Fe nucleus is given by

$$\delta(^{57}\text{Fe}) = \delta_0 - 0.7h_e \quad (14)$$

where $\delta(^{57}\text{Fe})$ is in mm/s, relative to $\alpha\text{-Fe}$ at room temperature, δ_0 is 1.68, 0.87, and 0.47 mm/s for the isolated Fe^{2+} , Fe^{3+} and Fe^{4+} , respectively.

The chemical surrounding factor for Cu(1) and Cu(2) site in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ crystal is obtained using Eq.(13), and the isomer shifts of Fe^{3+} and Fe^{4+} ions doped $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ were calculated from Eq.(14). The results are shown in Table II. The agreement between the calculated values and experimental values indicates that the Doublet's assignment of Mössbauer spectrum of $\text{Tl}_2\text{Ba}_2\text{Ca}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{10}$ in Ref.[3] is reasonable.

The measured Mössbauer spectrum shows that for less Fe-doped ($x=0.01$) sample, Fe occupies the site of

TABLE I Chemical bond parameters of $Tl_2Ba_2Ca_2Cu_3O_{10}$

Bondtype	$N_e^\mu/\text{\AA}^3$	k_F^μ	E_F^μ	E_h^μ/eV	C^μ/eV	f_c^μ	χ^μ/eV
TlO(3)	1.486	3.530	47.513	5.624	29.111	0.036	1.988
TlO(4)	0.325	2.127	17.251	3.773	11.637	0.095	3.103
BaO(2)	0.204	1.821	12.644	3.038	18.247	0.027	0.663
BaO(3)	0.115	1.504	8.625	3.182	13.637	0.052	0.625
BaO(4)	0.046	1.108	4.681	2.628	7.641	0.110	0.729
CaO(1)	0.222	1.873	13.380	3.930	21.368	0.033	0.455
CaO(2)	0.255	1.962	14.681	4.408	18.746	0.053	0.726
Cu(1)O(1)	1.024	3.118	37.074	7.831	6.923	0.561	13.007
Cu(2)O(2)	0.893	2.979	33.838	7.811	14.150	0.234	4.510
Cu(2)O(3)	0.239	1.921	14.072	4.178	3.834	0.543	9.999

TABLE II The relation between isomer shifts and chemical surrounding factors h_e in $Tl_2Ba_2Ca_2(Cu_{1-x}Fe_x)_3O_{10+\delta}$

Site	h_e	$\delta(\text{Fe}^{3+})/(\text{mm/s})$		$\delta(\text{Fe}^{4+})/(\text{mm/s})$	
		Clac.	Expt.[3]	Clac.	Expt.[3]
Cu(1)	0.890	0.247	0.25	-0.153	-0.17
Cu*(1)	1.090	0.107	0.15		
Cu(2)	0.794			-0.086	-0.06
Cu*(2)	1.021	0.156	0.14		

Cu(1) in the form of Fe^{3+} and Fe^{4+} , whose isomer shifts is 0.25 and -0.17 mm/s respectively. With increasing to $x=0.10$ of Fe-doped amount, a part of the Fe occupies the site of Cu(2) in the form of Fe^{4+} , and the measured isomer shifts is -0.06 mm/s. Since the valency of the iron ions is higher than that of the copper, extra oxygen may be present in the lattice. These oxygen atoms would probably tend to go into the Ca plane. The local trapping of the additional oxygen atoms can transform Cu(1)-O and Cu(2)-O cluster into Cu*(1) and Cu*(2) coordinated by 6 oxygen atoms. According to the estimated values of isomer shifts for Cu*(1) and Cu*(2) sites in Tl-2223 (see Table II), it is reasonable to assign the smaller peaks of $\delta=0.15$ of the sample with $x=0.01$ and $\delta=0.14$ of the sample with $x=0.10$ to Cu*(1) and Cu*(2) sites, respectively.

IV. CONCLUSIONS

Chemical bond properties of $Tl_2Ba_2Ca_2Cu_3O_{10}$ were studied by using the average band-gap model. The calculated results show that the covalency of Cu(1)-O bond is 0.561, the average covalency of Cu(2)-O is 0.296. The Mössbauer isomer shifts of ^{57}Fe in $Tl_2Ba_2Ca_2Cu_3O_{10}$ were calculated using the chemical surrounding factor, h_e , defined by the covalency and electronic polarizability. A very good agreement can be

found between theoretical results and the corresponding experimental data. It is verified that when lower doping, Fe substitute the Cu at the Cu(1) site in form of Fe^{3+} and Fe^{4+} ; when higher doping, Fe^{3+} and Fe^{4+} ion occupies Cu(1) and Cu(2) site respectively. This shows the chemical bond parameters calculated by us are reasonable. The results indicated that the chemical bond parameters play a main role in explaining the Mössbauer isomer shifts in high T_c superconductors.

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