I. INTRODUCTION

$\text{Tl}_2\text{Ba}_2\text{Ca}_n\text{Cu}_{3}\text{O}_{10}$ was reported to be a superconductor with a highest transition temperature of 125 K among the homologous series of $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$. The direct information on the Cu ion site at the atomic level is important for elucidating the superconductivity mechanism. The local bond properties of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ 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 $^{57}\text{Fe}$ in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ 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, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, Chemical bond, Mössbauer effect

II. THEORY AND CALCULATION

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

$$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} = \frac{1}{3}\text{TiO}(3) + \frac{5}{3}\text{TiO}(4) + \frac{8}{9}\text{BaO}(2) + \frac{8}{9}\text{BaO}(3) + \frac{2}{9}\text{BaO}(4) + \text{CaO}(1) + \text{CaO}(2) + \text{Cu}(1)\text{O}(1) + \frac{8}{5}\text{Cu}(2)\text{O}(2) + \frac{2}{5}\text{Cu}(2)\text{O}(3)$$

For any binary crystal $\text{AB}_n$ type compounds, consider shifts, which are strongly dependent on the local chemical environment of the Mössbauer nucleus [9-11]. In this work, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ has been investigated by considering all types of chemical bond. The chemical bond parameters and Mössbauer isomer shifts of Fe-doped in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ compound have been calculated. These results will contribute to a comprehensive understanding for high $T_c$ superconductivity mechanism.
erating symmetry, let the middle point between A and B atom as the origin of coordinate. The Hamiltonian is expressed as follows

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

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

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

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

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 $\mu$ bond $E_{g \mu}$ can be separated into homopolar $E_{h \mu}$ and heteropolar $C_{\mu}$ parts

$$(E_{g \mu})^2 = (E_{h \mu})^2 + (iC_{\mu})^2 \tag{4}$$

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

$$f_{L \mu} = \left( \frac{C_{\mu}}{E_{g \mu}} \right)^2, \quad f_{c \mu} = \left( \frac{E_{h \mu}}{E_{g \mu}} \right)^2 \tag{5}$$

$$E_{h \mu} = \frac{39.74}{(dn)^{2.48}} \tag{6}$$

$$C_{\mu} = \frac{14.4 \beta_{0} e^{-k_{\mu} r_{0 \mu}}}{r_{0 \mu}} [(Z_{A \mu})^* + \Delta Z_{A \mu} - n(Z_{B \mu})^*] \tag{7}$$

$$r_{0 \mu} = \frac{d_{\mu}}{2}, \quad k_{\mu} = \frac{4k_{F \mu} \beta_{0}}{\pi a_{B}} \tag{8}$$

$$\beta_{\mu} = 3\pi^2 n_{\mu} \tag{9}$$

where $\beta_{0}$ is the Bohr radius and $n$ is the ratio of element B to element A in the subformula ($n>1$). $\Delta Z_{A \mu}$ 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(II) and Cu(IIB) in square planar and pyramidal site, respectively. $k_{F \mu}$ is Fermi wave number of valence electron gas, $N_{\mu} \beta$ is the numbers of valence electrons of type $\mu$ bond per cubic centimeter, $b^2$ is proportional to the square of the average coordination number $N_{\mu} \beta$

$$b^2 = \beta (N_{\mu} \beta)^2 \tag{10}$$

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

$$\varepsilon(\infty) = 1 + \chi$$

$$= 1 + \frac{\hbar \Omega_{\mu}}{E_{F \mu}} \left[ 1 - \frac{E_{F \mu}}{4E_{F \mu}} + \frac{(E_{F \mu})^2}{48(E_{F \mu})^2} \right] \tag{11}$$

$$\varepsilon(\infty) - 1 = \chi = \sum_{\mu} F_{\mu} \chi$$

where, $\varepsilon(\infty)$ is dielectric constant of $\mu$ bond, $\chi$ is the macroscopic linear susceptibility, $\chi$ is the total macroscopic susceptibility, $E_{F \mu}$ is the Fermi energy, $\Omega_{\mu}$ is the plasma frequency, $F_{\mu}$ is the fraction of bonds of type $\mu$ composing the actual complex crystal.

Using the $\beta$ 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 $h_c$, has been proposed

$$h_c = \left( \sum_{\mu} \alpha_{L \mu} f_{c \mu} \right)^{1/2} \tag{13}$$

Where $\alpha_{L \mu}$ is the polarizability of the ligand bond volume in the $\mu$ bond. In recent work [10], it has been shown that linear relationships are observed between $h_c$ and the isomer shift $\delta$ for a specific ion. The isomer shift for $^{57}$Fe nucleus is given by

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

Where $\delta^{(57\text{Fe})}$ is in mm/s, relative to $\alpha$-Fe at room temperature, $\delta_0$ 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 Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ crystal is obtained using Eq.(13), and the isomer shifts of Fe$^{3+}$ and Fe$^{4+}$ ions doped Tl$_2$Ba$_2$Ca$_2$Cu$_3$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 Tl$_2$Ba$_2$Ca$_2$ (Cu$_{1-x}$Fe$_x$)$_3$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 Tl₂Ba₂Ca₂Cu₃O₁₀

<table>
<thead>
<tr>
<th>Bondtype</th>
<th>N_e/Å³</th>
<th>k_e²</th>
<th>E_p/Å³</th>
<th>E₁/eV</th>
<th>C₂/eV</th>
<th>f_c²</th>
<th>χ²/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>TlO(3)</td>
<td>1.486</td>
<td>3.530</td>
<td>47.513</td>
<td>5.624</td>
<td>29.111</td>
<td>0.036</td>
<td>1.988</td>
</tr>
<tr>
<td>TlO(4)</td>
<td>0.325</td>
<td>2.127</td>
<td>17.251</td>
<td>3.773</td>
<td>11.637</td>
<td>0.095</td>
<td>3.103</td>
</tr>
<tr>
<td>BaO(2)</td>
<td>0.204</td>
<td>1.821</td>
<td>12.644</td>
<td>3.038</td>
<td>18.247</td>
<td>0.027</td>
<td>0.663</td>
</tr>
<tr>
<td>BaO(3)</td>
<td>0.115</td>
<td>1.504</td>
<td>8.625</td>
<td>3.182</td>
<td>13.637</td>
<td>0.052</td>
<td>0.625</td>
</tr>
<tr>
<td>BaO(4)</td>
<td>0.046</td>
<td>1.108</td>
<td>4.681</td>
<td>2.628</td>
<td>7.641</td>
<td>0.110</td>
<td>0.729</td>
</tr>
<tr>
<td>CaO(1)</td>
<td>0.222</td>
<td>1.873</td>
<td>13.380</td>
<td>3.930</td>
<td>21.368</td>
<td>0.033</td>
<td>0.455</td>
</tr>
<tr>
<td>CaO(2)</td>
<td>0.255</td>
<td>1.962</td>
<td>14.681</td>
<td>4.408</td>
<td>18.746</td>
<td>0.053</td>
<td>0.726</td>
</tr>
<tr>
<td>Cu(1)O(1)</td>
<td>1.024</td>
<td>3.118</td>
<td>37.074</td>
<td>7.831</td>
<td>6.923</td>
<td>0.561</td>
<td>13.007</td>
</tr>
<tr>
<td>Cu(2)O(2)</td>
<td>0.893</td>
<td>2.979</td>
<td>33.838</td>
<td>7.811</td>
<td>14.150</td>
<td>0.234</td>
<td>4.510</td>
</tr>
</tbody>
</table>
| Cu(2)O(3)| 0.239  | 1.921| 14.072 | 4.178  | 3.834  | 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 Tl₂Ba₂Ca₂Cu₃O₁₀ [14], it is reasonable to assign the smaller peaks of δ = 0.15 of the sample with x = 0.01 and δ = 0.14 of the sample with x = 0.10 to Cu*(1) and Cu*(2) sites, respectively.

IV. CONCLUSIONS

Chemical bond properties of Tl₂Ba₂Ca₂Cu₃O₁₀ 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 ⁵⁷Fe in Tl₂Ba₂Ca₂Cu₃O₁₀ were calculated using the chemical surrounding factor, hₑ, 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 Fe³⁺ and Fe⁴⁺; when higher doping, Fe³⁺ and Fe⁴⁺ 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 Tc superconductors.

V. ACKNOWLEDGMENT

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