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Bonding and Mössbauer Isomer Shifts in (Tl, Pb) - 1223 Cuprate

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Abstract: By using the chemical bond theory of dielectric description, the chemical bond parameters of (Tl, Pb) - 1223 was calculated. The results show that the Sr-O, Tl-O, and Ca-O types of bond have higher ionic character and the Cu-O types of bond have more covalent character. Mössbauer isomer shifts of ^{57}Fe and ^{119}Sn doped in (Tl, Pb) -1223 were calculated by using the chemical environmental factor, h_e, defined by covalency and electronic polarizability. Four valence state tin and three valence iron sites were identified in ^{57}Fe, and ^{119}Sn doped (Tl, Pb) -1223 superconductor. We conclude that all of the Fe atoms substitute the Cu at square planar Cu (1) site, whereas Sn prefers to substitute the square pyramidal Cu (2) site.

Keywords: Chemical bond, Mössbauer isomer shift, superconductor.

The third member of the homologous series of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ (Tl-1223) was reported to be a superconductor at a transition temperature of 118 K[1]. The Tl-1223 compound is known as a suitable material for practical applications because it has high T_c and J_c values. The small spacing between the CuO_2 planes in Tl-1223 can avoid a large anisotropy in the superconducting properties, 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. A number of papers on Mössbauer spectroscopy have been reported[2]. Nevertheless, there are still controversies concerning the spectrum fits and the interpretation is conflictive. It is important that the local environment of specific ions is understood well. 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. The bond covalency theory was successfully generalized to multiple bond systems[3], and the method has been applied to Mössbauer isomer shift[4-6]. In this paper, Tl-1223 have been investigated by considering all types of chemical bond. The chemical bond parameters and Mössbauer isomer shifts have been calculated. These results will contribute to a comprehensive understanding of high T_c superconductivity mechanism.

Theory and Calculation

According to crystallographic data[1] and theoretical method[3], (Tl, Pb)-1223 can be decomposed into the sum of binary crystals as follows:

$$\begin{aligned}&(\mathrm{Tl, Pb})\, \mathrm{Sr_2Ca_2Cu_3O_{9-y}} = \mathrm{Tl\, Sr_2\, Ca_2\, Cu\,(1)\, Cu\,(2)_{\,2}\, O\,(1)_{\,4}\, O\,(2)_{\,2}\, O\,(3)_{\,2}\, O\,(4)_{\,1-y}}\\ &= \mathrm{Tl_{4\,(1-y)/(6-4y)}O\,(4)_{\,4\,(1-y)/6} + Tl_{2\,(1-y)/(6-4y)}O\,(3)_{\,2/6} + Sr_{8/(9-y)}O\,(1)_{\,8/6}}\\ &+ \mathrm{Sr_{8/(9-y)}O\,(3)_{\,8/6} + Sr_{2y/(9-y)}O\,(4)_{\,2(1-y)/6} + CaO\,(1)_{\,8/6} + CaO\,(2)_{\,8/6}}\\ &+ \mathrm{Cu\,(1)\,O\,(2)_{\,4/6} + Cu\,(2)_{\,8/5}O\,(1)_{\,8/6} + Cu\,(2)_{\,2/5}O\,(3)_{\,2/6}} \qquad (1)\end{aligned}$$

For any binary crystal AB_n type compounds, the average energy gap for every μ bond, E_g^{μ}, can be separated into homopolar, E_h^{μ}, and heteropolar, C^{μ}, parts

$$(E_g^{\mu})^2 = (E_h^{\mu})^2 + (C^{\mu})^2 \qquad (2)$$

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

$$f_i^{\mu} = (C^{\mu})^2 / (E_g^{\mu})^2$$

$$f_c^{\mu} = (E_h^{\mu})^2 / (E_g^{\mu})^2 \qquad (3)$$

Using the β value (0.1172) of Y-123 superconductor[5], the chemical bond parameters of each type of chemical bond are calculated , and listed in **Table 1** (d^{μ} is bond length), from which, we find that the Sr-O, Tl-O, and Ca-O types of bond have higher ionic character and the Cu-O types of bond have more covalent character.

Table 1 Chemical bond parameters of $(\mathrm{Tl_{0.5}, Pb_{0.5}})\,\mathrm{Sr_2Ca_2Cu_3O_{9-y}}$

Bond type	d^{μ} Å	E_h^{μ}, eV	C^{μ}, eV	f_c^{μ}
TlO (4)	2.710	3.353	7.034	0.185
TlO (3)	2.010	7.036	28.814	0.056
SrO (1)	2.655	3.528	22.012	0.025
SrO (3)	2.760	3.205	10.425	0.086
SrO (4)	2.633	3.602	22.472	0.025
CaO (2)	2.442	4.341	19.437	0.047
CaO (1)	2.509	4.059	18.271	0.047
Cu (1) O (2)	1.904	8.047	7.558	0.531
Cu (2) O (1)	1.906	8.026	14.730	0.229
Cu (2) O (3)	2.370	4.676	6.581	0.335

Mössbauer Isomer Shifts of ^{57}Fe and ^{119}Sn

As 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 coordination number, the covalency and the bond polarizability. So the chemical environmental factor designated by the symbol h_e, has been proposed

$$h_e = (\Sigma\ \alpha_L^{\mu} f_c^{\mu})^{1/2} \tag{4}$$

Where α_L^{μ} is the polarizability of the ion volume of the anion in the μ bond. The isomer shift for ^{57}Fe nucleus is given by[4,5]

$$\delta\ (^{57}\mathrm{Fe}) = \delta_0\text{-}0.7\ h_e\ (\text{mm/s, relative to } \alpha\text{-Fe at room temperature}) \tag{5}$$

where δ_0 is 1.68, 0.87, and 0.47 mm/s for the isolated Fe^{2+} ,Fe^{3+} and Fe^{4+} , respectively. The isomer shift for Sn^{4+} nucleus is given by[6]

$$\delta(^{119}\mathrm{Sn})=-0.69+1.14\ h_e\ (\text{mm/s, relative to } SnO_2 \text{ at room temperature}) \tag{6}$$

Table 2 Relation between δ and chemical environmental factors h_e in (Tl, Pb) -1223：Fe

site	h_e	$\delta_{calc.}$（Fe^{2+}）	$\delta_{calc.}$（Fe^{4+}）	$\delta_{calc.}$（Fe^{3+}）	$\delta_{expt.}$[7]	$\Delta_{expt.}$[7]	*RI* (%)[7]
Cu(1)	0.884	1.06	-0.15	0.25	0.24	1.36	72.1
Cu(2)	0.660	1.21	0.01	0.41			
Cu(1)	0.884			0.25	0.25	0.93	27.9

Table 3 Relation between δ and h_e in (Tl, Pb)-1223：Sn

site	h_e	$\delta_{calc.}$（Sn^{4+}）	$\delta_{expt.}$[7]	*RI* (%)[7]
Cu(1)	0.884	0.32		
Cu(2)	0.660	0.06	0.07	88.8
impurity			0.45	11.2

The chemical environmental factor for Cu site in (Tl, Pb) -1223 crystal is obtained using Eq. (4), and the isomer shifts of Fe^{n+}, and Sn^{4+}ions doped (Tl, Pb) -1223 were calculated from Eq. (5) and Eq. (6). The results are shown in **Table 2** and **Table 3**. In Ref. 7, two doublets have been used to fit the ^{57}Fe spectra at room temperature. They chose to assign the doublet D_1 with Δ=1.36 mm s^{-1} and δ=0.24 mm s^{-1} to Fe at the Cu(1) sites, and the doublet D_2 with Δ=0.93 mm s^{-1} and δ=0.25 mm s^{-1} to Fe at the Cu(2) sites. The relative spectral areas (*RI*) of the doublets D_1 and D_2 are 72.1%, and 27.9%, respectively. From **Table 2**, the high spin Fe^{3+} state substituting for Cu (1) ion was identified by comparing the calculated value of the isomer shifts with the experimental value of doublet D_1. But, the results we report here can not support the view that the doublet D_2 corresponds to Fe located in Cu (2) sites. We think that the doublet D_2 may be connected with iron atoms at the Cu′(1) site which is the sublattice originated from the statistical distribution[2] of the neighboring cations of Cu (1) site, *e.g.*, the partial substitution of Ca by Sr. Moreover, from **Table 3**, the calculated result clearly shows that the singlet with δ=0.07 mms^{-1}, correspond to Sn^{4+} located in the square pyramidal Cu (2) sites.

Conclusion

We started from the chemical bond viewpoint, investigated all constituent chemical bonds in Tl-1223 crystal, and the results show that the Sr-O, Tl-O, and Ca-O types of bond have higher ionic character and the Cu-O types of bond have more covalent character. Mössbauer isomer shifts of ^{57}Fe and ^{119}Sn doped in (Tl, Pb)-1223 were calculated by using the chemical environmental factor. A very good agreement between theoretical results and the corresponding experimental data was found. This shows the chemical bond parameters calculated by us are reasonable, and the chemical bond parameters play the main role in explaining the Mössbauer isomer shifts in high T_c superconductors. The determination of the correspondence between spectrum components (doublets) and actual copper sites occupied by Mössbauer nucleus was made easier with the aid of our calculated results of the chemical bond parameters.

References

1. J. K. Liang, G. C. Che, X. L. Chen, *The Phases Relation and the Crystal Structure in High* T_c *Oxide Superconductors* (in Chinese), Science Press, Beijing, **1994**, p. 171.
2. R. Z. Ma, Y. T. Xu, *Mössbauer Spectroscopy* (in Chinese), Beijing, Science Press, **1998**.
3. S. Y. Zhang, *Chin. J. Chem. Phys.* (in Chinese), **1991**, *4*, 109.
4. F. M. Gao, S. Y. Zhang, *Chin. J. Inorg. Chem.* (in Chinese), **2000**, *16*, 751.
5. F. M. Gao, D. C. Li, S. Y. Zhang, *J. Chin. Rare Earth Soc.* (in Chinese), **2001**, *19*, 209.
6. F. M. Gao, *Chin. J. Chem. Phys.* (in Chinese), **2000**, *13*, 673.
7. E. Kuzmann M. Mair, Z. Klencsar, A. Vertes, Z. Homonnay, G. Gritzner, *Physica C*, **1999**, *319*, 12.

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