Articles

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

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By using the chemical bond theory of dielectric description, the chemical bond parameters of （Hg，Pb）-1223 were calculated. The results show that the （Ba，Sr）-O and Ca—O types of bond have higher ionic character, while the Cu—O and （Hg，Pb）-O types of bond have more covalent character. Mössbauer isomer shifts of ^{57}Fe and ^{119}Sn doped in （Hg，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 （Hg，Pb）-1223 superconductor. It can be concluded 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

Introduction

The third member of the homologous series of Hg-$Ba_2Ca_{n-1}Cu_nO_{2n+2}$（Hg-1223）was reported to be a superconductor at the highest transition temperature of 133 K,[1] 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, compounds （Hg，Pb）-1223 were investigated by considering all types of chemical bond. The chemical bond parameters and Mössbauer isomer shifts were calculated. These results will contribute to a comprehensive understanding of high T_c superconductivity mechanism.

Theory method

According to the chemical bond theory of complex crystals,[3] the 'crystal formula' is a combination of chemical bond subformula. Since any chemical bond is binary, the bond subformula is also binary. The subformula of any kind of chemical bond A—B in the multibond crystal $A_aB_bD_dG_g\cdots$ can be expressed by the following formula

$$\left[\frac{N(B—A)a}{N_{CA}}\right] A \left[\frac{N(A—B)b}{N_{CB}}\right] B \qquad (1)$$

where A, B, D, G, $\cdots$ represent different elements or different sites of the same element in the crystal formula, and a, b, d, g, $\cdots$ represent numbers of the corresponding element. $N(B—A)$ represents the number of B ions in the coordination group of the A ion, and N_{CA} represents the nearest coordination number of A ion. 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

$$f_i^\mu = (C^\mu)^2/(E_g^\mu)^2$$
$$f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2 \qquad (3)$$

where

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \qquad (4)$$

$$C^\mu = 14.4b^\mu[(Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^*]e^{-k_s^\mu \cdot r_0^\mu}/r_0^\mu \qquad (5)$$
$$r_0^\mu = d^\mu/2$$

$$k_s^\mu = (4k_F^\mu/\pi a_B)^{1/2} \tag{6}$$

$$(k_F^\mu)^3 = 3\pi^2 N_e^\mu \tag{7}$$

where a_B is the Bohr radius and n is the ratio of element B to element A in the subformula. ΔZ_A^μ is the correction factor of d electron effect such as the crystal field stabilization energy and Jahn-Teller effect, etc.[4] k_F^μ is the Fermi wave number of valence electron gas, N_e^μ is the number of valence electrons of μ bond type per cubic centimeter, and b^μ is proportional to the square of the average coordination number N_c^μ.

$$b^\mu = \beta(N_c^\mu)^2 \tag{8}$$

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

$$\varepsilon^\mu(\infty) = 1 + \chi^\mu = 1 + (h\Omega_p^\mu/E_g^\mu)^2[1 - E_g^\mu/4E_F^\mu + (E_g^\mu)^2/48(E_F^\mu)^2] \tag{9}$$

$$\varepsilon(\infty) = 1 + \chi = \sum_\mu F^\mu \chi^\mu \tag{10}$$
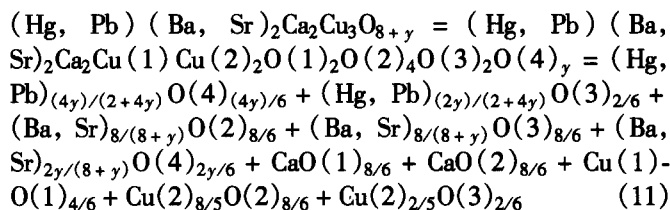
where, $\varepsilon^\mu(\infty)$ is the dielectric constant of μ bond, χ is the macroscopic linear susceptibility, χ^μ is the total macroscopic susceptibility of a binary crystal composed of only one type of μ bond, E_F^μ is Fermi energy, Ω_p^μ is the plasma frequency, and F^μ is the fraction of the binary crystal composing the actual complex crystal. The bond parameters of the crystal, of which the dielectric constant is unknown, may also be estimated by using the β value of an isostructural crystal.

Results and discussion

Bond parameters of (Hg, Pb)-1223

According to crystallographic data[1] and theoretical

method,[3] (Hg, Pb)-1223 can be decomposed into the sum of binary crystals as follows:

(Hg, Pb)(Ba, Sr)$_2$Ca$_2$Cu$_3$O$_{8+y}$ = (Hg, Pb)(Ba, Sr)$_2$Ca$_2$Cu(1)Cu(2)$_2$O(1)$_2$O(2)$_4$O(3)$_2$O(4)$_y$ = (Hg, Pb)$_{(4y)/(2+4y)}$O(4)$_{(4y)/6}$ + (Hg, Pb)$_{(2y)/(2+4y)}$O(3)$_{2/6}$ + (Ba, Sr)$_{8/(8+y)}$O(2)$_{8/6}$ + (Ba, Sr)$_{8/(8+y)}$O(3)$_{8/6}$ + (Ba, Sr)$_{2y/(8+y)}$O(4)$_{2y/6}$ + CaO(1)$_{8/6}$ + CaO(2)$_{8/6}$ + Cu(1)O(1)$_{4/6}$ + Cu(2)$_{8/5}$O(2)$_{8/6}$ + Cu(2)$_{2/5}$O(3)$_{2/6}$ (11)

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, It can be found that the (Ba, Sr)-O and Ca—O types of bond have higher ionic character and the Cu—O and (Hg, Pb)-O types of bond have more covalent character.

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 as

$$h_e = (\sum \alpha_L^\mu f_c^\mu)^{1/2} \tag{12}$$

where α_L^μ is the polarizability of the ion volume of the anion in the μ bond. For the μth bond, the polarizable coefficient α_0^μ can be obtained by Lorentz-Lorenz equation.

$$(\varepsilon^\mu - 1)/(\varepsilon^\mu + 2) = (4\pi/3)\alpha_0^\mu \tag{13}$$

the polarizability of the bond volume is

$$\alpha_b^\mu = \alpha_0^\mu \nu_b^\mu \tag{14}$$

Table 1 Chemical bond parameters of (Hg, Pb)-1223

Bond type	d^μ (10^{-1} nm)	N_e^μ	k_F^μ	E_h^μ (eV)	C^μ (eV)	f_c^μ	χ^μ	α_L^μ
(Hg, Pb)-O(4)	2.710	0.218	1.863	3.353	2.705	0.606	17.792	
(Hg, Pb)-O(3)	2.000	1.797	3.761	7.123	10.552	0.313	17.152	
(Ba, Sr)-O(2)	2.708	0.219	1.864	3.359	19.058	0.03	0.652	
(Ba, Sr)-O(3)	2.782	0.085	1.361	3.142	11.140	0.074	0.671	
(Ba, Sr)-O(4)	2.632	0.238	1.918	3.605	20.428	0.03	0.613	
Ca—O(1)	2.527	0.202	1.815	3.988	17.938	0.047	0.605	
Ca—O(2)	2.446	0.223	1.875	4.324	19.323	0.048	0.573	
Cu(1)—O(1)	1.916	0.926	3.016	7.923	7.389	0.535	10.864	0.375
Cu(2)—O(2)	1.918	0.769	2.835	7.902	14.109	0.239	3.830	0.290
Cu(2)—O(3)	2.460	0.292	2.052	4.263	6.535	0.298	6.314	0.672

the polarizabilities of the ion volume in μth bond are

$$\alpha_A^\mu = \{(r_A^\mu)^3/[(r_A^\mu)^3 + (r_B^\mu)^3]\}\alpha_o^\mu \qquad (15)$$

$$\alpha_B^\mu = \{(r_B^\mu)^3/[(r_A^\mu)^3 + (r_B^\mu)^3]\}\alpha_o^\mu \qquad (16)$$

where r_A^μ and r_B^μ are radii of atoms A and B in the μth bond, respectively.

The isomer shift for ^{57}Fe nucleus (mm/s, relative to α-Fe at room temperature) is given by[4,5]

$$\delta(^{57}\text{Fe}) = \delta_0 - 0.7h_e \qquad (17)$$

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 (mm/s, relative to SnO_2 at room temperature) is given by[6]

$$\delta(^{119}\text{Sn}) = -0.69 + 1.14h_e \qquad (18)$$

The chemical environmental factor for Cu site in (Hg, Pb)-1223 crystal is obtained using Eq. (16), and the isomer shifts of Fe^{n+} and Sn^{4+} ions doped (Hg, Pb)-1223 were calculated from Eqs. (17) and (18). The results are shown in Tables 2 and 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 the quadrupole spitting $\Delta = 1.42$ mm/s and isomer shift $\delta = 0.22$ mm/s to Fe at four-fold oxygen coordinated Cu(1) sites between the Ca layers in the (Hg, Pb)-1223 compound, and the doublet D_2 with $\Delta = 0.52$ mm/s and $\delta = 0.24$ mm/s to Fe at five-fold oxygen coordinated Cu(2) sites between the (Ba, Sr)-O and Ca layers. The relative spectral areas (RA) of the doublets D_1 and D_2 are 69.8%, and 30.2%, respectively.

Table 2 Relationship between isomer shifts δ and chemical environmental factors h_e in (Hg, Pb)-1223: Fe[a]

Site	h_e	δ_{calcd} (Fe^{2+})	δ_{calcd} (Fe^{4+})	δ_{calcd} (Fe^{3+})	δ_{expt}[7]	Δ_{expt}[7]	RA (%)[7]
Cu(1)	0.896	1.05	−0.16	0.24	0.22	1.42	69.8
Cu(2)	0.691	1.20	−0.01	0.39			
Cu'(1)	0.896			0.24	0.24	0.52	30.2

[a] Δ_{expt} is quadrupole splitting, RA is relative spectral areas.

Table 3 Relationship between isomer shifts δ and chemical environmental factors h_e in (Hg, Pb)-1223: Sn[a]

Site	h_e	δ_{calcd}(Sn^{4+})	δ_{expt}[7]	Δ_{expt}[7]	RA (%)[7]
Cu(1)	0.896	0.33			
Cu(2)	0.691	0.10	0.11		84.5
Impurity			0.45	1.42	15.5

[a] Δ_{expt} is quadrupole splitting, RA is relative spectral areas.

From Table 2, according to our calculated results, 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. This assignment is also based on the following considerations: (i) Fe has a well known site preference for the planar four-fold oxygen coordinated Cu(1) sites in the $YBa_2Cu_3O_7$ system;[2] (ii) the unusually high value of the quadrupole splitting ($\Delta = 1.42$ mm/s) refers to a very asymmetric spatial charge distribution around the Fe^{3+} cations. At this Cu(1) site, Fe should be in a distorted square planar four-fold oxygen coordination which would account for the obtained high quadrupole splitting value.

But, the results we report here can not support the view that the doublet D_2 corresponds to Fe located in Cu(2) sites. In Mössbauer spectroscopy study, some of the Mössbauer data for substituted compound have shown conclusively that the quadrupole splitting of an Fe^{3+} cation is dependent on the nearest-neighbour cation environment.[2] In this way, Mössbauer resonance lines of Fe ions in an equivalent site of crystals may be further splitted into multiple quadrupole doublets, and quadrupole splitting can be obtained as follows

$$\Delta = \alpha^2 \cdot F \cdot \Delta(0) \qquad (19)$$

where $\Delta(0)$ is the largest value of quadrupole splitting; α is valence factor, $\alpha = 1$ for ionic crystals, and $\alpha < 1$ for ionic-covalent crystals; F is reduced function of quadrupole splitting, and $F < 1$. According to this theory, 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 of the neighboring cations of Cu(1) site, *e. g.*, the partial substitution of Ca by Ba.

The ^{119}Sn Mössbauer results reflect two different microenvironments of Sn in the investigated sample.[7] Mössbauer parameters were listed in Table 3. Both isomer shifts correspond to Sn^{4+}. Based on consideration of ionic radii, the ions Sn^{4+} should be able to enter the Cu layers. According to our calculated results of the isomer shifts: we assign the larger component, the singlet, to Sn^{4+} in the Cu(2) sites. In fact, the square pyramidal Cu(2) site in (Hg, Pb)-1223 is very similar to the Cu(2) site in Y-123. In Y-123,[8] Sn atoms are also in the four valence and mainly replace Cu atoms in Cu(2) sites. The isomer shift and the quadrupole splitting of the minor component, the doublet, are unusually high compared to those of tetravalent tin compounds. Therefore, this doublet may be due to Sn incorporated in the impurity phase.

Conclusion

We started from the chemical bond viewpoint and investigated all constituent chemical bonds in (Hg, Pb)-1223 crystal. The results show that the (Ba, Sr)-O and Ca—O types of bond have higher ionic character and the Cu—O and (Hg, Pb)-O types of bond have more covalent character.

Mössbauer isomer shifts of ^{57}Fe and ^{119}Sn doped in (Hg, Pb)-1223 were calculated by using the chemical environmental factor. A very good agreement between theoretical results and the corresponding experimental data was observed. This shows the chemical bond parameters calculated by us are reasonable, and the chemical bond parameters play main roles 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　Liang, J.-K.; Che, G.-C.; Chen, X.-L. *The Phase Relation and the Crystal Structure in High T_c Oxide Superconductors*, Science Press, Beijing, **1994** (in Chinese).

2　Ma, R.-Z.; Xu, Y.-T. *Mössbauer Spectroscopy*, Science Press, Beijing, **1998** (in Chinese).

3　Zhang, S.-Y. *Chin. J. Chem. Phys*. **1991**, *4*, 109 (in Chinese).

4　Gao, F.-M.; Zhang, S.-Y. *Chin. J. Inorg. Chem*. **2000**, *16*, 751 (in Chinese).

5　Gao, F.-M.; Li, D.-C.; Zhang, S.-Y. *J. Chin. Rare Earth Soc*. **2001**, *19*, 209 (in Chinese).

6　Gao, F.-M. *Chin. J. Chem. Phys*. **2000**, *13*, 673 (in Chinese).

7　Kuzmann, E.; Mair, M.; Grttzner, G. *Physica C* **1999**, *312*, 45.

8　Chen, Y.-L.; Li, B.-R.; Chen, A; Xu, B.-F. *Hyperfine Interact*. **1990**, *55*, 1249.

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