

The bond ionicity in $\text{RBa}_2\text{Cu}_3\text{O}_7$ (R = Pr, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 L85

(<http://iopscience.iop.org/0953-8984/10/5/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 23:18

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

The bond ionicity in $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ ($\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}$)Q B Meng[†], Z J Wu and S Y Zhang

Laboratory of Rare Earth Inorganic Materials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 19 November 1997

Abstract. $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ ($\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}$) has been studied using complex chemical bond theory. The results indicated that with the decreasing of R radius, the ionicities for all considered types of bond decrease. This is in good agreement with the experimental fact that T_c decreases with the decreasing of R radius. $\text{Pr}\text{Ba}_2\text{Cu}_3\text{O}_7$ with no Ba-site Pr in this calculation is also predicted to be a superconductor. This supports the conclusion obtained by Blackstead *et al.* The ionicity for each bond obeys the following order: $\text{Ba}-\text{O} > \text{R}-\text{O} > \text{Cu}(2)-\text{O}(1) > \text{Cu}(2)-\text{O}(2,3) > \text{Cu}(1)-\text{O}(4) \sim \text{Cu}(1)-\text{O}(1)$.

It is known that rare earth R substitution for Y in $\text{Y}\text{Ba}_2\text{Cu}_3\text{O}_7$ (YBCO) has little effect on superconductivity, namely, T_c only slightly decreases with the decreasing radius of R [1], and also relatively little change is observed in the cell constant [2]. However, the puzzle that the superconductivity is also suppressed in Pr-based compound ($\text{Pr}\text{Ba}_2\text{Cu}_3\text{O}_7$) [2, 3], which has the same orthorhombic structure as YBCO, has attracted much interest [4] from the viewpoint of understanding the basic mechanisms of high- T_c superconductivity in copper oxides. From the analysis of the experimental results, the suppression of superconductivity in PBCO has received different explanations, for example, the variety of valences of Pr ions [5, 6], the magnetic pair-breaking mechanism [7], charge compensation (hole-filling) [8, 9], the Abrikosov–Gorkov pair-breaking model [10] and so on. On the other hand, Blackstead *et al* [11] have reported the observation of inhomogeneous superconductivity with a critical temperature $T_c \approx 92$ K in PBCO and given an explanation that this is because of the substitution of Pr for Y, and not for Ba (no Ba-site Pr) in their PBCO crystal. It is well known that the concept of ionicity has often played an important role for explaining and classifying many basic properties of molecules and solids from the viewpoint of electronic structure [12–15], and, up to now, only a little attention has been paid to this aspect [16]. In that work [16], the bond ionicities of a series of compounds were investigated, but, for each compound, only three types of bond were considered, and even the three types of bond were artificially restricted in a box. The objective of this investigation is to study $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ ($\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}$) by considering all types of chemical bond (11 in total) using the complex chemical bond theory [17], which is the development of Phillips, Van Vechten and Levine (PVL) [12–15] and has been successfully applied to many fields [17–21].

It is known that PV [13, 14] theory can only deal with binary crystals, especially A^NB^{8-N} type. Although theory which can deal with more complex crystals, such as AB_n and A_mB_n

[†] Present address: State Key Laboratory for Surface Physics, Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China.

types of crystal, successfully had been developed by Levine [15], for ABC_2 , ABC_3 and ABC_4 types of crystal, however, an explicit expression was not given to decompose the complex multibond crystals into binary crystals. Therefore, it is worthwhile to extend these fruitful ideas. After considering these ideas in chemical bond representation, we succeeded in generalizing PVL theory for multibond systems [17–19]. Using this generalized theory, any complex crystal can be decomposed into a sum of binary crystals. These obtained binary crystals are related to each other and every binary crystal includes only one type of chemical bond, but the properties of these binary crystals are different from those of the real corresponding binary crystal (if any), although its chemical bond parameters can be calculated in the similar way.

Suppose A denotes cations and B anions, any multibond complex crystal can be written as $A_{a_1}^1 A_{a_2}^2 \dots A_{a_i}^i \dots B_{b_1}^1 B_{b_2}^2 \dots B_{b_j}^j$, where A^i and B^j represent the different elements of the different sites of a given element of cations and anions respectively, and a_i and b_j represent the numbers of the corresponding elements. Thus, together with crystal structure data, the crystal can be decomposed into binary crystals by the following formula:

$$A_{a_1}^1 A_{a_2}^2 \dots A_{a_i}^i \dots B_{b_1}^1 B_{b_2}^2 \dots B_{b_j}^j = \sum_{i,j} A_{m_i}^i B_{n_j}^j \quad (1)$$

$$m_i = N(B^j - A^i)a_i/N_{CA_i} \quad n_j = N(A^i - B^j)b_j/N_{CB_j} \quad (2)$$

where N_{CA_i} and N_{CB_j} represent the nearest total coordination numbers of A^i and B^j ions in the crystal. $N(B^j - A^i)$ represents the nearest coordination fraction contributed by A^i ions, and $N(A^i - B^j)$ has similar meaning. After decomposing the complex crystal into different kinds of binary crystal, which are isotropic systems and introducing the concept of effective valence electron, PVL theory can be directly applied to the calculation of the chemical bond parameters in complex crystals.

Table 1. The ionicity (%) of each bond in $RBa_2Cu_3O_7$ (R = Y, Pr, Sm, Eu, Gd, Dy, Ho, Er, Tm).

	Pr	Sm	Eu	Gd	Dy	Ho	Y	Er	Tm
Ba–O(1)	94.62	94.60	94.60	94.56	94.57	94.57	94.56	94.54	94.48
Ba–O(2)	94.67	94.65	94.65	94.62	94.63	94.63	94.63	94.61	94.54
Ba–O(3)	94.67	94.65	94.65	94.62	94.63	94.63	94.62	94.61	94.54
Ba–O(4)	94.66	94.64	94.64	94.60	94.62	94.62	94.61	94.59	94.54
R–O(2)	93.78	93.75	93.75	93.70	93.71	93.71	93.70	93.68	93.46
R–O(3)	93.78	93.75	93.75	93.70	93.71	93.71	93.70	93.67	93.46
Cu(1)–O(1)	79.43	79.55	79.59	79.22	79.45	79.49	79.44	79.42	79.13
Cu(1)–O(4)	79.84	79.77	79.76	79.65	79.67	79.68	79.66	79.58	79.39
Cu(2)–O(1)	86.53	86.48	86.48	86.35	86.40	86.41	86.39	86.36	86.16
Cu(2)–O(2)	81.24	81.17	81.15	81.02	81.02	81.04	81.01	81.04	80.77
Cu(2)–O(3)	81.24	81.17	81.16	81.08	81.08	81.09	81.08	81.00	80.82

The crystal structure data of $RBa_2Cu_3O_7$ (R = Pr, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm) are taken from [2]. The positions of all the atoms in $RBa_2Cu_3O_7$ crystal structure are similar to that of $YBa_2Cu_3O_7$. Based on complex crystal chemical bond theory, the multibond complex crystals $RBa_2Cu_3O_7$ (R = Pr, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm) can be decomposed into binary crystals which contain only one type of bond each. The compositions of different binary crystals are

$$\begin{aligned}
 \text{RBa}_2\text{Cu}_3\text{O}_7 &= \text{RBa}_2\text{Cu}(1)\text{Cu}(2)_2\text{O}(1)_2\text{O}(2)_2\text{O}(3)_2\text{O}(4)_1 = \text{Ba}_{4/5}\text{O}(1)_{4/3} + \text{Ba}_{2/5}\text{O}(2)_{2/3} \\
 &+ \text{Ba}_{2/5}\text{O}(3)_{2/3} + \text{Ba}_{2/5}\text{O}(4)_{2/3} + \text{R}_{1/2}\text{O}(2)_{2/3} + \text{R}_{1/2}\text{O}(3)_{2/3} \\
 &+ \text{Cu}(1)_{1/2}\text{O}(4)_{1/3} + \text{Cu}(1)_{1/2}\text{O}(1)_{1/3} + \text{Cu}(2)_{2/5}\text{O}(1)_{1/3} \\
 &+ \text{Cu}(2)_{4/5}\text{O}(2)_{2/3} + \text{Cu}(2)_{4/5}\text{O}(3)_{2/3}.
 \end{aligned}$$

The calculated results of ionicities in $\text{RBa}_2\text{Cu}_3\text{O}_7$ ($\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Y}, \text{Er}, \text{Tm}$) for each type of bond are listed in table 1 and all of the 11 types of chemical bond can be divided into two groups. The first are Ba–O and R–O types of bond, which have higher ionic characters; the second are Cu–O types of bond, which have more covalent character in each bond. It is seen that the ionicities of Cu(2)–O(2) and Cu(2)–O(3) in YBCO are 81.01 and 81.08% respectively, in good agreement with those of Tanaka [16], which give 81.80% (average value of the ionicities of Cu(2)–O(2) and Cu(2)–O(3)). In addition, for in-plane oxygen and neighbouring (out-of-plane) cations, that is, Ba–O(2), Ba–O(3), Y–O(2) and Y–O(3) in our labels, the bond ionicity was slightly overestimated in Tanaka's work, in which it is 98.2%, whereas in our case it is about 94.2% in YBCO (arithmetic average values of the four bonds). However, for the bond ionicities of metal–apical oxygen, that is, Cu(2)–O(1) in our labels, an unrealistic result was obtained in Tanaka's study, 99.8%, while in our calculation it is 86.4%. This suggests that our results show reasonable values in ionicities for the bonds of Ba–O(2), Ba–O(3), Y–O(2), Y–O(3) and Cu(2)–O(1). The reason that leads to the unrealistic results in Tanaka's work may be that only three types of bond were considered and these were artificially restricted in a box. Since it is experimentally known that T_c decreases with decreasing radius of R [1], it is very interesting to see that the ionicity of each bond also follows this order: this may indicate that large ionicity is preferred in superconductivity. The ionicities of these chemical bonds also show an interesting picture that the fragments with stronger covalence (CuO_2 plane and Cu–O chain) are embedded in higher-ionicity fragments (BaO, RO). From our results it is also instructive to note that since the ionicities of PBCO are similar to those of the other RBCO, PBCO should be a superconductor in our case. This is not surprising because Pr in our calculations only substitutes the Y position (no Ba-site Pr): this is in good agreement with the conclusions delivered by Blackstead *et al* [11]. The ordering of ionicity for each bond have the sequence, Ba–O > R–O > Cu(2)–O(1) > Cu(2)–O(2,3) > Cu(1)–O(4) ~ Cu(1)–O(1).

References

- [1] Lin J G, Huang C Y, Xue Y Y, Chu C W, Cao X W and Ho J C 1995 *Phys. Rev. B* **51** 12900
- [2] Le Page Y, Siegrist T, Sunshine S A, Schneemeyer L F, Murphy D W, Zahurak S M, Waszczak J V, Mckinnon W R, Tarascon J M, Hull G W and Greene L H 1987 *Phys. Rev. B* **36** 3617
- [3] Schneemeyer L F, Waszczak J V, Zahurak S M, Van Dover R B and Siegrist T 1987 *Mater. Res. Bull.* **22** 1467
- [4] Radousky H B 1992 *J. Mater. Res.* **7** 1917
- [5] Dalichaouch Y, Torikachvili M S, Early E A, Lee B W, Seaman C L, Yang K N, Zhou H and Maple M B 1988 *Solid State Commun.* **65** 1001
- [6] Hilscher G, Holland-Moritz E, Holubar T, Jostarndt H-D, Nekvasil V, Schaudy G, Walter U and Fillion G 1994 *Phys. Rev. B* **49** 535
- [7] Guo G Y and Temmerman W M 1990 *Phys. Rev. B* **41** 6372
- [8] Cao G, O'Reilly J W, Crow J E, Kennedy R J and Pernambuco-Wise P 1993 *Physica B* **186–188** 1004
- [9] Reyes A P, MacLaughlin D E, Takigawa M, Hammel P C, Heffner R H, Thompson J D, Crow J E, Kebede A, Mihalisin T and Schwegler J 1990 *Phys. Rev. B* **42** 2688
- [10] Kebede A, Jee C S, Schwegler J, Crow J E, Mihalisin T, Myer G H, Salomon R E, Schlottmann P, Kuric M V, Bloom S H and Guerin R P 1989 *Phys. Rev. B* **40** 4453

- [11] Blackstead H A, Dow J D, Chrisey D B, Horwitz J S, Black M A, McGinn P J, Klunzinger A E and Pulling D B 1996 *Phys. Rev. B* **54** 6122
- [12] Pauling L 1960 *The Nature of the Chemical Bond* 3rd edn (Ithica, NY: Cornell University Press)
- [13] Phillips J C 1970 *Rev. Mod. Phys.* **42** 317
- [14] Phillips J C and Van Vechten J A 1969 *Phys. Rev. Lett.* **22** 705
- [15] Levine B F 1973 *J. Chem. Phys.* **59** 1463
- [16] Tanaka S 1994 *Physica C* **220** 341
- [17] Zhang S 1991 *Chin. J. Chem. Phys.* **4** 109
- [18] Xue D and Zhang S 1996 *J. Phys.: Condens. Matter* **8** 1949
- [19] Meng Q B, Wu Z J and Zhang S Y *J. Phys. Chem. Solids* at press
- [20] Gao F and Zhang S 1994 *Acta Chim. Sin.* **52** 320
- [21] Zhang S 1995 *J. Rare Earths* **13** 85