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Correlations among c/b, T_c, and Madelung potentials in the system of $RBa_2Cu_3O_x$ superconductors

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We have observed a correlation between the lattice-constant ratio c/b and T_c in R-Ba-Cu-O superconductors (where R is a rare-earth element). Madelung potentials and the bond length of Cu(1)—O(3) are calculated and correlated with the distribution of T_c over the various $RBa_2Cu_3O_7$ superconductors. Further consideration of $YBa_2Cu_3O_x$ with variable x of suitable oxygen content leads to an explanation of the correlation of decreasing c/b ratio with increasing T_c. A Coulomb-type ionic mechanism is therefore suggested so that shortening of the c axis and increased chain length provides (1) a channel of charge-transfer excitation from chain to Cu-O layers and (2) a long-range Coulomb interaction between the two Cu-O layers, both of which result in stronger coupling between the two Cu-O layers and higher T_c.

Since Chu and Wu[1] and their collaborators first discovered in 1987 the superconductor $YBa_2Cu_3O_7$ with high transition temperature T_c, many studies of the Y-Ba-Cu-O quaternary system have been performed in order to attempt to understand the underlying mechanism of superconductivity. Research on $YBa_2Cu_3O_x$ concerning the correlation between T_c and crystal structure have proceeded along two routes: one by varying the oxygen content $(6<x<7)$, and the other by replacing Y with other rare-earth elements, viz. $RBa_2Cu_3O_x$. For example, the T_c dependence of the lattice constants of the unit cell (a, b, and c),[2,3] upon the distortion $\frac{1}{3}c-a$,[4] upon the unit-cell volume,[3,4] the orthorhombic splitting, $(b-a)/a$ etc., has shown that small structural changes and the critical temperature T_c of the superconducting phase of $YBa_2Cu_3O_x$ are related. We report now the c/b ratio for various cases of $RBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ $(6<x<7)$. To explore why the ratio c/b is so strongly correlated with T_c, we have calculated the Madelung potential of $RBa_2Cu_3O_7$. It is found that the variation of Madelung potentials among superconductors with different R is similar to that of the bond length of Cu(1)—O(3). The calculation and description are given in detail. Finally, we discuss why the Coulomb interaction plays so important a role and draw conclusions from this.

We follow the notation of Ref. 5 for various ion positions in the structure of $YBa_2Cu_3O_x$ and use the values of their lattice parameters. Cu(1) and O(1) are in the chain direction (b axis); with O(2) the vacant position (a axis); O(3) in the c axis (apex of the pyramid of the Cu site); and Cu(2)-O(4)-O(5) as the copper oxide layer. We note that samples of the same composition can be prepared, via different processes, to exhibit different T_c values.[6] Thus we make comparisons and analyses of data from the laboratory[5] that provides the most complete data of the $RBa_2Cu_3O_7$ system. We find that for the samples $RBa_2Cu_3O_x$ from each of the laboratories investigated,[5,7–9] the ratio c/b always tends to decrease as T_c increases. As shown in Fig. 1, the variations in the c/b ratio are of the order of magnitude of 0.001. Consequently, the validity of the correlation between c/b and T_c depends mainly on the accuracy of measurement of the lattice constants but also on the quality of the sample. As displayed in Table I, which was obtained from the data from seven papers by Takita and co-workers,[5] with quite accurate measurements, we analyzed these different $RBa_2Cu_3O_7$ samples on the relation between c/b and T_c. The result, shown in Fig. 1, correlates the T_c at midpoint and at zero resistivity with the c/b ratio, via the series of samples of substitutional replacement of the rare-earth (R) element. The relation is clear that T_c increases with decreasing c/b

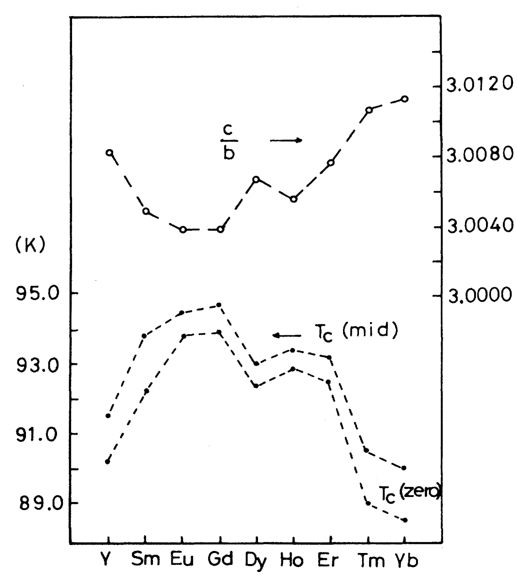

FIG. 1. The c/b ratio and T_c in the $RBa_2Cu_3O_7$ system, R being the rare-earth element.

TABLE I. The lattice parameters of $RBa_2Cu_3O_x$ and their T_c, T_c width, ΔT_c, and the bond length of Cu(1)–O(3) (see Ref. 5).

	a (Å)	b (Å)	c (Å)	T_c(mid) (K)	ΔT_c (K)	$d_{Cu(1)-O(3)}$ (Å)
Y	3.8179(1)	3.8828(1)	11.6809(3)	91.5	2.5	1.849
Sm	3.8440(1)	3.9018(2)	11.7248(4)	93.8	3.0	1.872
Eu	3.8384(2)	3.8973(3)	11.7069(8)	94.5	1.3	1.851
Gd	3.8350(2)	3.8947(2)	11.6992(6)	94.7	1.5	1.885
Dy	3.8246(1)	3.8865(1)	11.6857(3)	93.0	1.2	1.794
Ho	3.8192(1)	3.8850(1)	11.6770(2)	93.4	1.0	1.918
Er	3.8128(1)	3.8781(1)	11.6644(3)	93.2	1.4	1.836
Tm	3.8087(1)	3.8746(2)	11.6655(6)	90.5	3.0	1.820
Yb	3.8018(2)	3.8710(2)	11.6576(5)	90.0	3.0	1.838

and vice versa. The relation between c/b and T_c is accordingly depicted in Fig. 2(a), where the T_c's at each midpoint T_c(mid) and their widths ΔT_c are shown.

A similar relation is also found in the $YBa_2Cu_3O_x$ superconductors with variable oxygen content. Based on experimental findings,[10] higher oxygen content gives higher T_c, a gradual decrease in the lattice constant c, and a slight increase in the lattice constant b. The net result is a decreasing c/b with increasing T_c, as displayed in Fig. 2(b). The widths ΔT_c are also indicated similarly, as in Fig. 2(a). Taking into consideration both the results of Figs. 2(a) and 2(b), we find in both cases an increasing T_c with decreasing c/b. In the comparison we further found the correlation is more pronounced when the lattice constants are known more accurately. We also tried to relate the c/a ratio to T_c, but did not find such a good correlation as c/b with T_c. In order to understand the close relation between c/b and T_c, we proceeded to calculate the Madelung potential for the system of the $RBa_2Cu_3O_7$ superconductors.

The valences of Y^{3+} and Ba^{2+} in the $YBa_2Cu_3O_x$ system ($x = 6$–7) have been generally accepted. It is also known that $YBa_2Cu_3O_x$ is an ionic insulator when $x = 6$, but is metallic when $x > 6.5$. However, its charge-carrier concentration ($\sim 10^{21}$ cm^{-3}) in the metallic phase is so low that one can assume a high ionicity in $YBa_2Cu_3O_x$ and deal with an ionic model. In such a crystal, the long-range Coulombic interactions (Madelung potential energy) contribute dominantly to the total potential of the ions

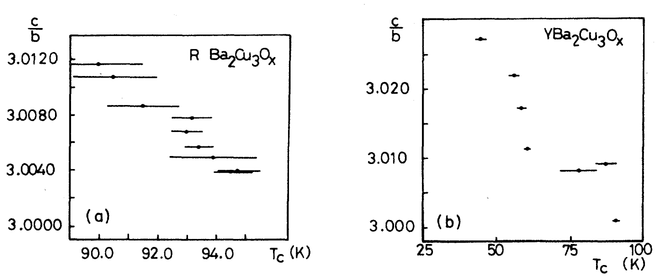

FIG. 2. (a) The c/b ratio dependence of T_c in the $RBa_2Cu_3O_x$ system. (b) The c/b ratio dependence of T_c in $YBa_2Cu_3O_x$ with variable oxygen contents ($6 < x < 7$).

(over 80% of the total potential, although they vary with the ionicity).[11,12] The mechanically repulsive interactions between nearest ions also contribute to some extent, but are found to be small compared with Coulombic interactions. We neglect contributions from the repulsive interactions and also van der Waal's attractive interaction in this work. We remark further that our Madelung-potential calculation, treating only the relative effect arising from substitutional replacement of the R element in $RBa_2Cu_3O_7$ rather than treating a general Madelung problem, is expected to yield more accurate and meaningful predictions.

Next, we calculated the Madelung potential per $YBa_2Cu_3O_7$ "molecule" (i.e., formula unit) according to the well-known Ewald's method.[13] The desired total potential of the reference ion i in the field of all the other ions in the crystal is

$$\psi(i) = \frac{4\pi}{\Delta}\sum_{\mathbf{G}} S(\mathbf{G})G^{-2}\exp\left(\frac{G^2}{4}\right) - 2q_i\left(\frac{\eta}{\pi}\right)^{1/2} + \sum_j \frac{q_j}{r_j}F(\eta^{1/2}r_j)\,, \quad (1)$$

where Δ is the volume of the unit cell, $\mathbf{G}$ is the reciprocal lattice vector and η is a control parameter which allows both sums of Eq. (1) to converge rapidly. The functions $F(x)$ and $S(\mathbf{G})$ are defined, respectively, as

$$F(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-S^2}ds\,,$$

$$S(\mathbf{G}) = \sum_j q_j \exp(i\mathbf{G}\cdot\mathbf{r}_j)\,,$$

in which $S(\mathbf{G})$ is the structure factor of the crystal. Based on the condition of electric neutrality and some experimental results,[14] we assume that there are one Cu^{3+} at the Cu(1) site, two Cu^{2+} at the two equivalent Cu(2) sites, and vacancies at the O(2) sites. In Table II we show the Madelung energies for various ions in the $RBa_2Cu_3O_7$ molecule (R = Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb). The total Madelung potential energy which is the sum of all the ions in the molecule is shown in Fig. 3(a). Now we compare the total Madelung potentials with the sum of the Madelung potentials of Cu(1) and O(3) as shown in Fig. 3(b). The variation of the total Madelung potential

TABLE II. Madelung potential of each ion and the total Madelung potential of a $RBa_2Cu_3O_7$ unit cell (units in eV). In obtaining the total Madelung potential, the values of Ba, Cu(2), O(3), O(4), and O(5) are each doubled due to the symmetry of the unit cell of $RBa_2Cu_3O_7$.

	Y	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb
Cu(1)	−88.701	−89.162	−90.136	−87.777	−91.889	−85.322	−90.669	−91.295	−92.100
Cu(2)	−58.139	−57.657	−57.428	−58.210	−57.293	−58.862	−57.615	−57.527	−57.258
R	−100.142	−94.544	−94.189	−94.873	−101.315	−99.522	−97.913	−97.819	−94.251
Ba	−34.390	−35.386	−35.524	−35.414	−33.967	−34.761	−35.045	−35.058	−36.048
O(1)	−54.161	−53.188	−52.888	−53.970	−52.984	−55.289	−53.165	−53.001	−52.367
O(3)	−46.987	−45.696	−45.641	−45.545	−47.928	−45.824	−46.512	−46.677	−45.649
O(4)	−37.584	−37.935	−38.290	−37.819	−37.838	−37.295	−38.410	−38.550	−39.359
O(5)	−37.392	−38.016	−38.344	−37.701	−37.488	−37.138	−38.254	−38.275	−39.015
Total	−335.996	−333.138	−333.837	−333.003	−337.593	−333.968	−336.712	−337.147	−336.691

with various *R* elements has very clearly the same tendency as the sum of the Madelung potentials of Cu(1) and O(3). This implies that the sum of the potential of Cu(1) and O(3) mainly reflects the variation of the total Madelung energy. The dominance suggests a correlation between the Madelung potential and the bond length of Cu(1)−O(3) because of the nature of Coulombic interaction. In fact, $DyBa_2Cu_3O_7$ has the smallest total Madelung potential, the smallest potential sum of Cu(1) and O(3), and also the smallest bond length of Cu(1)−O(3). On the other hand, $HoBa_2Cu_3O_7$ has relatively larger total Madelung potential, largest Cu(1) and O(3) Madelung potential sum, and largest bond length of

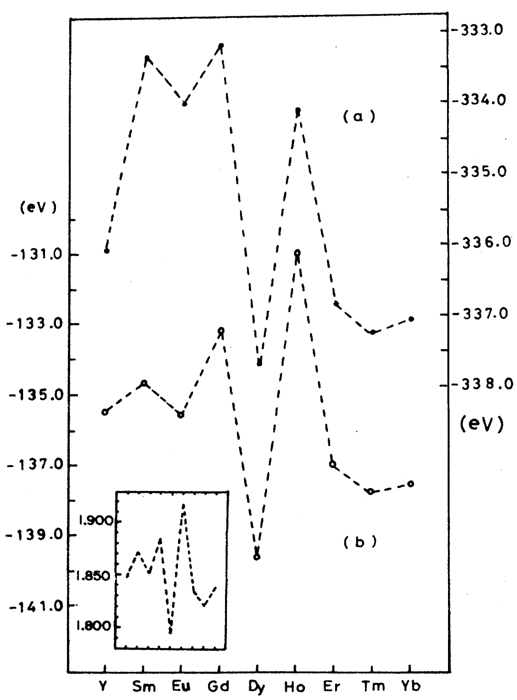

FIG. 3. (a) The total Madelung potential (eV) of $RBa_2Cu_3O_7$. (b) The sum of the Madelung potentials (eV) of Cu(1) and O(3) of $RBa_2Cu_3O_7$. The inset represents the bond length of Cu(1)−O(3) in the $RBa_2Cu_3O_x$. The abscissa is the same as in the main part of the figure.

Cu(1)−O(3). These are manifested in Figs. 3(a) and 3(b), and in the inset of the figure, respectively. Thus, the total Madelung potential energy of $RBa_2Cu_3O_7$ is quantitatively correlated to the bond length of Cu(1)−O(3).

Now we turn back to T_c of Fig. 1 and compare T_c with the total Madelung potential of Fig. 3(a). There exists the same tendency in the variations over the superconductors with different *R* elements except Sm and Tm for which the cause, while not known for certain, might be due to some individual feature of the ions themselves. Aside from this small discrepancy we have observed a consistent correlation among these quantities. A decrease in c/b is correlated to an increase in T_c, Madelung total potential, Madelung potential sum of Cu(1) and O(3), and the bond length of Cu(1)−O(3).

Having obtained the correlation among those quantities from substitutional replacement of the *R* element in $RBa_2Cu_3O_7$, we reconsider the situation of $YBa_2Cu_3O_x$ with variable oxygen content. The experimental result[15] is that greater oxygen content will cause longer bond length of Cu(1)−O(3), and thus shorter bond length of Cu(2)−O(3). This can be explained qualitatively from our concept of the ionic model due to Coulomb interaction. As oxygen content is increased, the occupation probability of O(1) sites would be increased. This would increase the length of the *b* axis. The bond length of Cu(1)−O(3) would be increased due to the Coulomb repulsive force on O(3) by O(1) and possibly the presence of O(2). The reaction force from O(3) would further repel O(1) and lengthen the *b* axis. As O(3) is pushed toward Cu(2) the increase in the Coulomb attraction between O(3) and Cu(2) would make Cu(2) come closer to O(3) such that the overall *c* axis is shrunk. Thus the ionic Coulomb interaction as displayed by using increasing oxygen content tends to yield a decreasing c/b, increasing bond length Cu(1)−O(3), increasing Madelung potential, and increasing T_c. During the process of decreasing in c/b, etc., there could be charge transfer excitation and simultaneously long-range Coulomb interaction between the two Cu-O layers. This therefore suggests a Coulombic mechanism that, increasing chain length and decreasing the *c* axis provides: (i) a channel of charge transfer[16,17] from the chain to the Cu-O layers and (ii) a long-range Coulomb interaction between the two Cu-O layers, both of which result in stronger coupling between the two Cu-O layers and higher T_c. The part of the superconductivity mechanism occurring within the Cu-O layers, which still exists there, is not addressed. To summarize, we first observed the correlation between the ratio c/b and T_c. Then we calculated the total Madelung potentials, the sum of Madelung potentials of Cu(1) and O(3), and also the bond length of Cu(1)−O(3) for the various $RBa_2Cu_3O_7$ superconductors. Comparison of these calculated results with the distribution of T_c over these superconductors shows a correlation between the bond length of Cu(1)−O(3) and T_c. On the other hand, still using the ionic Coulomb interaction (i.e., the same physics of Madelung potentials) but considering the superconductors $YBa_2Cu_3O_x$ with variable x, we explain the experimental result of decreasing c/b ratio with increasing oxygen content and increasing T_c.

To conclude, a correlation between c/b and T_c has been observed and explained. Consequently, a Coulomb-type charge-transfer excitation mechanism is suggested that, as a result of decreasing c and increasing b, charge transfer from chain to copper-oxide layers could happen and simultaneously a long-range Coulomb interaction between the two Cu-O layers could prevail, resulting in enhanced coupling between the two Cu-O layers and higher T_c.

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