

Study of Perovskite and Cuprate Crystallographic Structures of High T_c Superconductors



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ABSTRACT

In this paper, we have studied the perovskite and cuprate crystallographic structure of high T_c super conductors. We know that the majority of single element crystal have highly symmetrical structure, generally fcc or bcc in which their physical properties are the same along the three crystallographic dimensions x, y and z. The NaCl type and A15 compounds are also cubic. Some compounds do have lower symmetric, showing that superconductivity is compatible with many different types of crystallographic structure, but higher symmetric are certainly more common. The structure of high temperature superconductors, almost all of which are tetragonal or orthorhombic. The structure plays very important role in determining the property of superconductors. The higher T_c is alloys of transitions metal are at the boundaries of resistibility between bcc and hep forms. Almost all the high-temperature oxide superconductors have point symmetry D_{4h} ($a = b$) or symmetry close to D_{4h} ($a \ll b$). These superconductors consists of horizontal layers, each of which contains one positive ion and either zero, one or two oxygen. The copper ions may be coordinated square planar, pyramidal, or octahedral, with some additional distortion. Copper oxide layers are never adjacent. The captions alternate sites vertically as do the oxygen. The copper oxide layers are either flat or slightly puckered, in contrast to the other metal oxide layers, which are generally far from planar. The highest T_c compounds have metal layers (e.g. Ca) with no oxygen between the Copper Oxide planes.

Keywords :- Perovskite Structure, Cuprate Structure, High T_c Super Conductors, Super Conductivity, Tetragonal, Lattice Constant.

I. INTRODUCTION

In this paper, we have studied the perovskite and cuprate crystallographic structure of high T_c super conductors. We know that the majority of single element crystal have highly symmetrical structure, generally fcc or bcc in which their physical properties are the same along the three crystallographic dimensions x, y and z. The NaCl type and A15 compounds are also cubic. Some compounds do have

lower symmetric, showing that superconductivity is compatible with many different types of crystallographic structure, but higher symmetric are certainly more common. The structure of high temperature superconductors, almost all of which are tetragonal or orthorhombic. The structure plays very important role in determining the property of superconductors. The higher T_c is alloys of transitions metal are at the boundaries of resistibility between

bcc and hep forms. The NaCl type compounds have ordered valencies on one or another lattice site.

One begin with a description of perovskite and explain some reasons that perovskite undergoes various types of distortions. The prototype exhibits a number of characteristic that are common to the high-temperature superconducting cuprates emphasize the structural commonalities of these materials and make frequent comparison between them. The earlier work of the comprehensive review by Yvon and Francois⁶ has given more structural detail on the atom positions; inter atomic spacings, site symmetries, etc of these compounds. There have been reports of superconductivity in certain other suprate structure⁷.

There is a related of layered compounds $\text{Bi}_2\text{O}_2(\text{M}_{m-1}\text{R}_m\text{O}_{3m+1})$ called Aurivillius with the 12-coordinated $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Bi}, \text{Pb}, \text{Cd}, \text{La}, \text{Sm}, \text{Sc}, \text{etc}$, and the 6-coordinated transition metal $\text{R} = \text{Nb}, \text{Ti}, \text{Ta}, \text{W}, \text{Fe}, \text{etc}$. The $\text{M}=1$ compound Bi_2NbO_6 belongs to the same tetragonal space group $14/mmm$. D_{4h} as the lanthanum, bismuth and thallium high temperature superconductors⁴.

One assumes that all samples are well made and safety tored. Humidity can effect composition, and Garland⁵ found that storage of $\text{YB}_2\text{Cu}_1\text{O}_7$ in 98% humidity exponentially decreased the diamagnetic susceptibility with a time constant of 22 days.

II. METHODS AND MATERIAL

PEROVSKITES

Much high temperature superconductors been written about the being perovskites types, so one beings by describing the structure of perovskites. The prototype compound barium titanale, BaTiO_3 , exists in three crystallographic forms with the following lattice constants and unit cell volume⁶.

Cubic :	$a=b=c= 4.0118 \text{ \AA}$	$V = 64.57 \text{ \AA}^3$
Tetragonal :	$a=b= 3.9947, c=4.0336$	$V = 64.37 \text{ \AA}^3$
Orthorhombic :	$a= 4.009 \sqrt{2} \text{ \AA}, b= 4.018\sqrt{2} \text{ \AA}, c=3.990 \text{ \AA}$	$V = 2(64.2) \text{ \AA}^3$

For all three cases the crystallographic axes are mutually represent perpendicular.

CUBIC FORM

Above 201°C barium titanate is cubic and the until cell contains one formula unit BaTiO_3 with a titanium atom on each apex, a barium atom in the body centre of each edge of the cube. This corresponds to the barium atoms, titanium atom, and three oxygen atoms being placed in positions with the following x, y and z coordinates:

F Site : T_1	$(0,0,0)$	T_1 on apx
F Site : O	$(0,0,1/2), (0,1/2,0), (1/2,0,0)$	three oxygen centered on edges
C Site : Ba	$(1/2,1/2,1/2)$	Ba in centre

The Barium in the centre has 12 nearest neighbour, so we say that it is 12-fold coordinated, while the titanium on each apes has 6-fold (octadral) coordination with the oxygen, as may be seen. The notation E for edges, F for Face, and C for centre is adopted for reasons that will becomes clear in the discussion which follows. Throughout this paper we will assume that he z-axis is oriented vertically so that the x and y axes lie in the horizontal plane.

This structure is best understood in terms of the sizes of the atoms involved. The ionic radii of O^{2-} (1.32A) and Ba^{2+} (1.34A) are almost the same, as indicated in Table T₁ and together they form a perfect fcc lattice with the smaller Ti^{4+} ions (0.68A) located in octahedral holes surrounded entirely by oxygen. The octahedral holes of a close-packed oxygen lattice have a radius of 0.545A ; if these holes were empty the lattice constant would be: $a=3.73 \text{ A}$. pushes the surrounding oxygen outward thereby increasing the lattice constant. When the titanium is replaced by a

larger atom, the lattice constant expands further, as indicated by the data in the last column of Table T₂. When Ba is replaced by the smaller Ca (0.99 Å) and Sr (1.12 Å) ions, by contrast, there is a corresponding decrease in the lattice constant, as indicated by the data in column 3 and 4, respectively, of Table T₂. All three alkaline earths, Ca, Sr, and Ba appear prominently in the structure of 3 high temperature superconductors.

TETRAGONAL FORM

At room temperature barium titanate is tetragonal and the deviation from cubic, $(c-a) / (c+a)$, is

about 1%. All of the atoms have the z-axis relative to each other by $\ll 0.1$ Å producing the puckered arrangement. The distortions from the ideal structure are exaggerated in this sketch. The puckering bends then Ti-O-Ti group so that the Ti-O distance increase while the Ti-Ti distance remains almost the same. This has the effect of providing more room for the titanium atoms to fit in their lattice sites. One sees later than a similar puckering distortion occurs in the high-temperature superconductors as a way of providing space for the Cu atoms in the planes.

TABLE 1. Ionic Radii For Selected Elements

Small	Cu ²⁺	0.96 Å	Y ³⁺	0.94 Å	
Medium					
		Bi ³⁺	0.96	Tl ³⁺	0.95 Å
		Ca ²⁺	0.99 Å	Bi ³⁺	0.96 Å
		Nd ³⁺	0.995 Å		
Medium		Hg ²⁺	1.10 Å		
Large	Sr ²⁺	1.12 Å	La ³⁺	1.14 Å	
		Pb ²⁺	1.20 Å	Ag ⁺	1.26 Å
Large	K ⁺	1.33 Å	O ²⁻	1.32 Å	
		Ba ²⁺	1.34 Å	F ⁻	1.33 Å

Table 2. Dependence of lattice constants a of selected Perovskites AMO₃ on Alkaline Earth A and Ionic Radius of Transition Metal Ion M⁺⁴ the alkaline Earth Ionic Radii are 0.99 Å (Ca), 1.12 Å (Sr), and 1.34 Å (Ba)

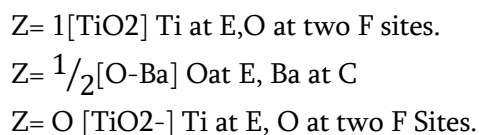
Transitional Metal	Transitional Metal radius, Å	Lattice constant a, Å		
		Ca	Sr	Ba
Ti	0.68	3.84	3.91	4.01
Fe	-	-	3.87	4.01
Mo	0.70	-	3.98	4.04
Sn	0.71	3.92	4.03	4.12
Zr	0.79	4.02	4.10	4.19
Pb	0.84	-	-	4.27
Ce	0.94	3.85	3.85	4.40
Th	1.02	4.37	4.37	4.80

ORTHORHOMBIC FORM

There are two principal ways in which a tetragonal structure distorts to form an orthorhombic phase. The first is for the b-axis to stretch relative to the a-axis, resulting in the formation of a rectangle. The second, shown at the bottom of the figure, is for one diagonal of the ab square to stretch and the other diagonal to compress, resulting in the formation of rhombus. The two diagonals are perpendicular, rotated by 45° relative to the original axes, and become the a¹, b¹ dimensions of the new orthorhombic unit cell. These a¹, b¹ lattice constants are = √2 times longer than the original constants, so that the volume of the unit cell roughly doubles, thus, it contains exactly twice as many atoms. (the same √2 factor appears in our discussion of the lattice constants for the orthorhombic form of barium titanate.) The transformation from tetragonal to orthorhombic is generally of the rhombus type for (La_{1-x}Sr_x)CuO₄ and of the rectangular type for YBa₂Cu₃O_{7-δ}.

III. PLANAR REPRESENTATION

Another way of picturing the structure of perovskite is to think of the atoms as forming horizontal planes. If we adopt the notation (E.F.C) to design the occupation of the E, F and C sites, the sketches of perovskite presented as.



The plane at the heights z=0, 1/2 and 1 can be labeled using this notation.

The completes the treatment of the structure of perovskite. One encountered many features that one meet again in the analogous superconductor cases and established notation that is useful in describing the structure of the cuprate.

IV. CRYSTAL CHEMISTRY

One briefly described the structure of some classical superconductors, and in this paper we provided a more detailed discussion of the structures of the cuprate superconductors. The questions arises of how structure is related to the presence of metallic and superconducting properties.

Villars and Phillips proposed to explain the combination of elements in compounds that are favorable for superconductivity at relatively high temperature by assigning three metallic coordinates to each atom, namely an electron number N_e, a size r and an electro-negativity X. The electron number are given for most of the elements with N_e=3 for all of the rare earth and actinide; several correlations of N_e and T_c have been already studied. The size and electro negativities were determined empirically from a study of some 3,000 binary inter metallic compounds of types AB, AB₂, AB₃, and A₂B₅. The resulting values for each atom together with their electron numbers. These values although arrived at empirically on the basis of the constraint of self consistency, do have a spectroscopic basis and thus are called, respectively, spectroscopic radii and spectroscopic electro negativities. The metallic coordinates of the atoms can be employed to calculate the three Villars-Phillips (VP) coordinates for each compound, namely (a) average number of valence electron N_v = <N_e>_{av}, (b) spectroscopic electro negative difference ΔX and (c) spectroscopic radius difference ΔR, where we are using the VP notation. For example, for the compound NbN, with T_c = 17.3 K using the data one has.

$$\begin{aligned} N_v &= \frac{1}{2}(4 + 5) = 4.5 \\ \Delta R &= 2.76 - 0.54 = 2.22 \\ \Delta X &= 2.03 - 2.85 = -0.82 \end{aligned}$$

The VP coordinates for the A15 compound Ge₃Nb with T_c = 23.2K calculated as follows:

$$N_V = \frac{1}{4} (4 + 3 \times 5) = 4.75$$

$$\Delta R = \frac{1}{2} (1.56 - 2.76) = -0.60$$

$$\Delta X = \frac{1}{2} (1.99 - 2.03) = -0.02$$

The text by Phillips tabulates the P coordinates for more the 60 superconductors with $T_c > 10K$ and for about 600 additional superconductors with transition temperatures in the range $1 < T_c < 10K$.

One has discussed the Phillips approach to crystal chemistry explanation of the superconductivity of the cuprates. Other researchers have offered alternate in some cases somewhat related, approaches to understanding the commonalities of the varieties of the various high temperature and classical superconductors.

V. COMPARISON WITH CLASSICAL SUPERCONDUCTOR STRUCTURES

Many elements such as copper and lead are face centered cubic, while many other elements, such as niobium, are body centered cubic, with $a = 3.30\text{\AA}$ for Nb A15 compounds, such as Nb_3Se are simple cubic with lattice constant $a \approx 3.63\sqrt{2}$ and have parallel chains of Nb atoms 5.14\AA apart. Other types of classical superconductors, such as the Laves and Chevrel phases, are cubic or close to cubic. The new oxide superconductors are tetragonal orthorhombic close to tetragonal, and they all have $a \approx b \approx 3.85\text{\AA}$, which is somewhat greater than the value for the A15 compounds. The third lattice constant c varies with the compound, with the values 13.2\AA for $LaSrCuO$, 11.7\AA for $YBaCuO$ and ≈ 23 to 36\AA for the $BiSrCaCuO$ and $TlBaCaCuO$ compounds. These differences occur because the number of copper-oxygen and other planes per unit cell, as well as the spacing between them, vary from compound to compound due to the diverse arrangement of atoms between the layer. Thus relatively high-symmetry crystal structures are characteristic of many superconductors.

VI. DISCUSSION OF RESULTS

Almost all the high-temperature oxide superconductors have point symmetry D_{4h} ($a = b$) or symmetry close to D_{4h} ($a \ll b$). These superconductors consist of horizontal layers, each of which contains one positive ion and either zero, one or two oxygen. The copper ions may be coordinated square planar, pyramidal, or octahedral, with some additional distortion. Copper oxide layers are never adjacent. The cations alternate sites vertically as do the oxygen. The copper oxide layers are either flat or slightly puckered, in contrast to the other metal oxide layers, which are generally far from planar. The highest T_c compounds have metal layers (e.g. Ca) with no oxygen between the Copper Oxide planes.

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