ORDER-DISORDER MECHANISM AND A PHENOMENOLOGICAL MODEL IN (Bi, Pb)–Sr–Ca–Cu–O

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We established a relationship between the structures of the bismuth high T_c superconducting compounds and a symmetry of disordered perovskite type. This description which we propose, leads to considering the structures of these materials in terms of a commensurate superstructure obtained from a latent perovskite structure of space group $Im3m$. A phenomenological model was elaborated in order to describe the two types of modulations realized in these compounds.

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1. Introduction

One of the essential and not totally resolved problems regarding the high T_c superconductor materials concerns the determination of their crystallochemical structure. The structural characterization of these compounds is difficult for many reasons. Among them can be first mentioned the relatively large number of atoms in one lattice. Nevertheless, this research can go forward if we notice that all common high T_c superconductor compounds, till now, possess elements of a common structure, in the family of perovskites [1].

Thus, in this paper, the structure element which is the common denominator to all considered compounds, is taken as the starting point from which several superconductor structures are obtained. In particular, we show that in the case of superconductor lanthane and bismuth oxides, their structure can be derived from cubic disordered perovskite structure whose space group is $Im3m$.

Let us consider for example the non-stoichiometric compound $Na_{0.75}WO_3$ of the family of Na_xWO_3, the corresponding lattice has eight chemical formulas $8(Na_{0.75}WO_3) = Na_6W_8O_{24}$. The space group is $Im3m$ [2]. This lattice can be

built by juxtaposition of eight disordered perovskite elementary lattices of space group $Pm3m$ in which the crystallographic sites are occupied as follows:

Na and vacancies in position $(0, 0, 0)$,

W in position $(1/2, 1/2, 1/2)$,

O in position $(1/2, 1/2, 0), (1/2, 0, 1/2), (0, 1/2, 1/2)$.

Therefore, we can consider the transition $Pm3m \rightarrow Im3m$ in which the minimization of Landau energy leads to two stable solutions [2]. This transition is an order-disorder type since the atoms and vacancies of sodium occupy different crystallographic positions in the cubic lattice P.

2. The $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ family

We can take a similar approach and show that we can go from a disordered cubic structure of space group $Im3m$ to describe the different phases (2201), (2212), (2223) of the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ family [3].

Concerning the (2201) phase (Fig. 1), the tetragonal structure can be obtained by multiplying the disordered cubic structure (Fig. 2) by five. The atoms

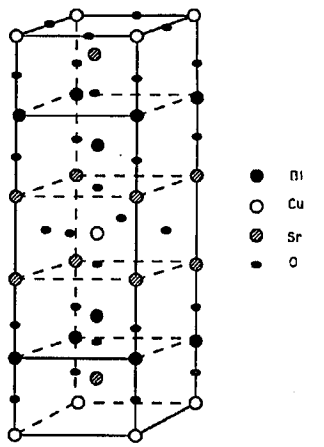

Fig. 1. Structure of (2201) phase.

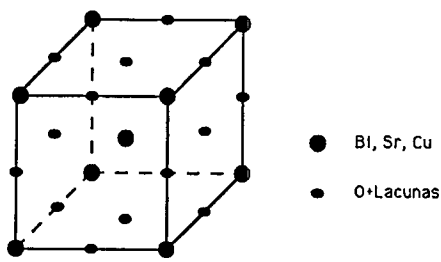

Fig. 2. Disordered cubic structure.

in the disordered cubic elementary structure are in these positions: Bi, Cu, Sr in position (0,0,0), (1/2,1/2,1/2); O and vacancies in positions (1/2,0,0), (0,1/2,0), (0,0,1/2), (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0). By multiplying the elementary structure by five, the atoms in the ordered tetragonal lattice come in positions:

Bi(4e)	(00z),(00z),(1/2 1/2 1/2+z),(1/2 1/2 1/2–z)
Cu(2a)	(000),(1/2 1/2 1/2),
Sr(4e)	(00z),(00z),(1/2 1/2 1/2+z), (1/2 1/2 1/2–z),
O(1)(4c)	(0 1/2 0),(1/2 0 0),(1/2 0 1/2), (0 1/2 1/2),
O(2)(4e)	(00z)...
O(3)(4e)	(00z')...

This leads us to the chemical formula: $Bi_4Sr_4Cu_2O_{12} = 2(Bi_2Sr_2Cu_1O_6)$ which corresponds clearly to the (2201) phase.

In the same way, the tetragonal structures of (2212) and (2223) can be obtained by multiplying the elementary disordered cubic structure by 7 and 9 respectively.

We can consider the $Im3m \rightarrow I4/mmm$ transition for the three phases. The primitive translations of the cubic structure I are

$$t_1 = a/2\ a/2\ -a/2, \quad t_2 = -a/2\ a/2\ a/2, \quad t_3 = a/2\ -a/2\ a/2.$$

For the (2201) phase, the primitive translations and the new translations are

$$t'_1 = a/2\ a/2\ 5a/2 = t_1 + 3t_2 + 3t_3, \quad t'_2 = a/2\ a/2\ -5a/2 = t_1 - 2t_2 - 3t_3,$$

$$t'_3 = a/2\ -a/2\ -5a/2 = -3t_2 - 2t_3.$$

For the (2212) phase

$$t'_1 = a/2\ a/2\ 7a/2 = t_1 + 4t_2 + 4t_3, \quad t'_2 = a/2\ a/2\ -7a/2 = t_1 - 3t_2 - 3t_3,$$

$$t'_3 = a/2\ -a/2\ -7a/2 = -4t_2 - 3t_3.$$

For the (2223) phase

$$t'_1 = a/2\ a/2\ 9a/2 = t_1 + 5t_2 + 5t_3, \quad t'_2 = a/2\ a/2\ -9a/2 = t_1 - 4t_2 - 4t_3,$$

$$t'_3 = a/2\ -a/2\ -9a/2 = -5t_2 - 4t_3.$$

The point of the Brillouin zone associated to the transition is the Δ point [2]. A generalization can be made to the bismuth oxide family, in which the volume would be multiplied by $2n + 3$. The positions of atoms in the disordered structure ($Im3m$): (Bi+Cu+Sr+Ca)(2a) (0,0,0), (1/2,1/2,1/2) and O+lacunes(6b) (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0), (1/2,0,0), (0,1/2,0), (0,0,1/2).

The positions of atoms in the ordered structure ($I4/mmm$):

(2201)	(2212)	(2223)
Cu(2a)(000)...	Cu(4e)(00z)...	Cu(1)(2a)(000)...
Bi(4e)(00z)...	Bi(4e)(00z)...	Cu(2)(4a)(00z)...
		Bi(4e)(900z)...
Sr(4e)(00z)...	Sr(4e)(00z)...	Sr(4e)(00z)...
	Ca(2b)(001/2)...	Ca(4e)(00z)...
O(1)(4c)(1/200)...	O(1)(8g)(01/2z)...	O(1)(4c)(1/200)...
O(2)(4e)(00z)...	O(2)(4e)(00z)...	O(2)(8g)(01/2z)...
O(3)(4e)(00z)...	O(3)(4e)(00z)...	O(3)(4e)(00z)...
		O(4)(4e)(00z)...

3. Phenomenological model

As we know, the superconductor phases (2212) and (2223) of bismuth oxide of the (Bi, Pb)–Sr–Ca–Cu–O have an orthorhombic average structure ($a = b =$ 5.4 Å, $c = 30.8$ Å and 37 Å respectively) of space group $Bbmb$ [4]. Their real structure is incommensurate with a wave vector modulation $q_1 = \delta_1 b^* + c^*$ ($\delta_1 =$ 0.21). Furthermore, in case of substitution by lead, a new modulation is involved with a wave vector $q_2 = \delta_2 b^*$ which coexists with the modulation of pure bismuth compound [5].

As mentioned above, the average structure of the bismuth compound is orthorhombic. As a matter of fact, the parameters a and b of the lattice are nearly equal. Consequently, the structure is pseudo-tetragonal, and if we refer to the first studies [3], the space group is $I4/mmm$ with $a = b = 3.8$ Å and $c = 30.7$ Å for the (2212) phase. As a result, we have been able to develop a model which consists of starting from the tetragonal phase of $I4/mmm$ space group to an orthorhombic phase of $Amaa$ space group.

This procedure consists of starting from a tetragonal lattice, and specifying the subgroup of low symmetry associated to the different points of high symmetry of the tetragonal I Brillouin zone. If we consider the point $X = (\pi/a\ \pi/a\ 0)$ of the Brillouin zone for example, the subgroups of low symmetry induced by several irreducible representations of $I4/mmm$ are:

$(Cmmm; P4/mmm)(\tau_1)$, $(Cccm; P4/nnm)(\tau_2)$, $(Cmca; P4/ncm)(\tau_3)$,

$(Cmca; P4/mbm)(\tau_4)$, $(Ccca; P4/nbm)(\tau_5)$, $(Cmma; P4/mcm)(\tau_6)$,

$(Cmcm; P4/mnm)(\tau_7)$, $(Cmcm; P4/nmm)(\tau_8)$ [2].

The different τ_i indicate the irreducible representations wherever several groups are associated to a τ_i. This means that there could be many stable solutions for the groups of low symmetry.

As we can see, it is possible to obtain the $Cccm$ group from $I4/mmm$. This group is equivalent to $Amaa$ by taking into consideration the permutations between (a, b, c). We present below the associated symmetry changes.

Tetragonal I primitive translations:

$$t_1 = (a/2, a/2, c/2), \quad t_2 = (a/2, a/2, -c/2), \quad t_3 = (a/2, -a/2, -c/2).$$

Orthorhombic A primitive translations:

$$t'_1 = -t_3 = (-a/2, a/2, c/2) = (0, b'/2, c'/2),$$
$$t'_2 = -t_1 + t_2 - t_3 = (-a/2, a/2, -c/2) = (0, b'/2, -c'/2),$$
$$t'_3 = t_1 + t_2 = (a, a, 0) = (a', 0, 0).$$

Concerning the bismuth type modulation, $q_1 = \delta_1 b^* + c^*$, if we refer to the tetragonal lattice, the q_1 extremity is located on the surface of the Brillouin zone near Z. The changes of the symmetry translations are:

$$t'_1 = t_1 + t_3 = (a, 0, 0) = (a', 0, 0),$$
$$t'_2 = t_2 - t_3 = (0, a, 0) = (0, b', 0) \quad \text{tetragonal } P(X) \text{ or orthorhombic } P(X),$$
$$t'_3 = t_1 - t_2 = (0, 0, c) = (0, 0, c'),$$

or

$$t'_1 = t_2 - t_3 = (0, a, 0) = (a'/2, b'/2, 0),$$
$$t'_2 = t_1 + t_3 = (a, 0, 0) = (a'/2, -b'/2, 0) \quad \text{orthorhombic } C(XY),$$
$$t'_3 = t_1 - t_2 = (0, 0, c) = (0, 0, c').$$

The primitive lattice of low symmetry is confounded with the conventional tetragonal lattice. We can determine the symmetry of bismuth atoms displacements in this lattice, which induce the group of low symmetry. We determined displacements which are transformed by the $I4/mmm$ symmetry operations like an irreducible representation of the Z point. We find as displacement type (Bi type) (Fig. 3):

$$(X1 + X2 - X3 - X4) + (Y1 + Y2 - Y3 - Y4) + (Z1 - Z2 + Z3 - Z4),$$
$$(X1 + X2 - X3 - X4) - (Y1 + Y2 - Y3 - Y4) + (Z1 - Z2 + Z3 - Z4),$$

are transformed as $(\tau_5)(Z)$,

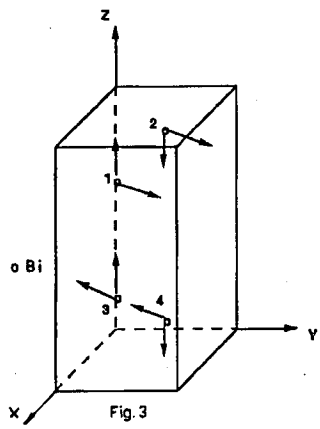

Fig. 3

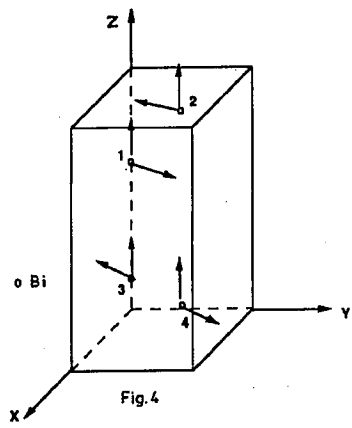

Fig. 4

Fig. 3. Displacements of bismuth atoms (Bi type).
Fig. 4 Displacements of bismuth atoms (Pb type).

$$(X1 - X2 + X3 - X4) + (Y1 - Y2 + Y3 - Y4) + (Z1 - Z2 + Z3 - Z4),$$

$$(X1 - X2 + X3 - X4) - (Y1 - Y2 + Y3 - Y4) + (Z1 - Z2 + Z3 - Z4)$$

are transformed as $(\tau_{10})(Z)$.

Concerning the second modulation $q_2 = \delta_2 b^*$ (Pb type) near Γ, the displacements are (Fig. 4):

$$(X1 - X2 - X3 + X4) + (Y1 - Y2 - Y3 + Y4) + (Z1 + Z2 + Z3 + Z4),$$

$$(X1 - X2 - X3 + X4) - (Y1 - Y2 - Y3 + Y4) + (Z1 + Z2 + Z3 + Z4)$$

are transformed as $(\tau_5)(\Gamma)$. The displacements involve a symmetry change $I4/mmm \rightarrow Amaa$.

4. Conclusion

In this paper, we established a relationship between the structures of the bismuth high T_c superconducting compounds and a symmetry of disordered perovskite type. The structural transition is realized through an order-disorder mechanism, which is followed by atoms displacements in the case of bismuth compound. This description which we propose, leads to consider the structures of those materials in terms of commensurate superstructure from a perovskite cubic latent structure of space group $Im3m$. Experimental proof attesting this model remains to be obtained. However, we can notice that a direct consequence of this mechanism would be that the superstructure parameter remains temperature independent. This consequence is actually realized, since the electron diffraction studies [6] show that the superstructure parameter is temperature independent.

The displacements of bismuth atoms, which we were able to determine, in order to describe the two type of modulations realized in these compounds, were used in the simulation of images, whereby the results obtained are consistent with observations in high resolution electron microscopy [7].

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