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Refinement of the Modulated Structures of Pb-Free and Pb-Doped Bi-2223 HTSC

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The incommensurate modulated structures of Pb-free and Pb-doped Bi-2223 phases were refined on single-crystal X-ray diffraction data.

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1. Introduction

Among the members of the high-temperature superconducting Bi-based family $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (n = 1, 2, 3), the three-layer compound $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) is the most attracting one, because of its high critical temperature 110 K, better transport properties, and potential industrial applications. However, it is difficult to synthesize the Bi-2223 phase, even at the laboratory scale. Partial substitution of Pb for Bi facilitates the synthesis, improves the stability, and enhances the superconducting properties. Due to oxygen off-stoichiometry and differences in the translation periods of the atom layers, the real crystal structures of these compounds are complex and exhibit incommensurate modulations (see [1] and references therein). Commensurate approximants of $Bi_2Sr_2CuO_{6+\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2201 and Bi-2212, respectively) have been refined on single-crystal diffraction data (e.g. [2, 3]) and the incommensurate structures have been refined in superspace (e.g. [4, 5]). However, the structure of Bi-2223 had not yet been refined, because of the lack of high-quality single crystals.

2. Experimental details

Single crystals were grown by the vapor-assisted travelling solvent floating zone method [6, 7] from samples having the nominal compositions $Bi_{2.1}Sr_{1.9}Ca_2Cu_3O_{10+\delta}$ and $Bi_{1.84}Pb_{0.32}Sr_{1.84}Ca_{1.97}Cu_3O_{10+\delta}$ ($Bi_{2.16}Pb_{0.26}Sr_{2.08}Ca_{1.95}Cu_{2.55}O_{10+\delta}$ from EDX analysis). Diffraction data were collected on a Stoe IPDS II diffractometer equipped with Mo K_α radiation, a graphite monochromator, and an imaging plate. The modulation was found to be incommensurate with $q = 0.206(5)a^*$ for Pb-free and $q = 0.20a^*$ for Pb-substituted Bi-2223, i.e. in a rough approximation commensurate with a vector $q = 0.2a^*$. The reflections could be indexed in a satisfactory way assuming large primitive orthorhombic cells, which correspond to 5-fold supercells of the conventional side-face centered orthorhombic cells. The structures

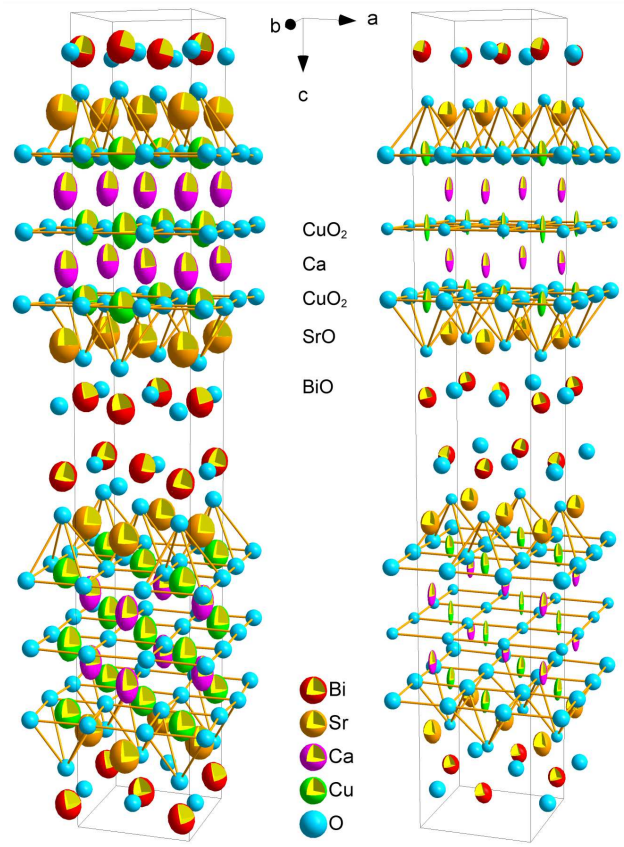

Fig. 1. Crystal structures of $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (left) and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ (right) (sequence of atom layers indicated); the atoms are represented by their displacement ellipsoids.

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were refined by the full-matrix least-squares method based on F, using the program package WinCSD [8].

3. Results

The average structures were refined in the orthorhombic space group $A2aa$ with the cell parameters $a = 5.4210(7)$, $b = 5.4133(6)$ and $c = 37.010(7)$ Å for the Pb-free phase, and $a = 5.3952(14)$, $b = 5.4130(10)$ and $c = 37.042(11)$ Å for the Pb-doped phase. The Bi site was split into two positions, the two partly occupied sites showing the largest difference in the x coordinates, in agreement with a modulation along a. The commensurate approximant superstructures were refined in the orthorhombic space group $Pnnn$, using a 5-fold supercell (5886 reflections with $I > 2\sigma(I)$ and 302 refined parameters). An additional oxygen site within the BiO layers was identified.

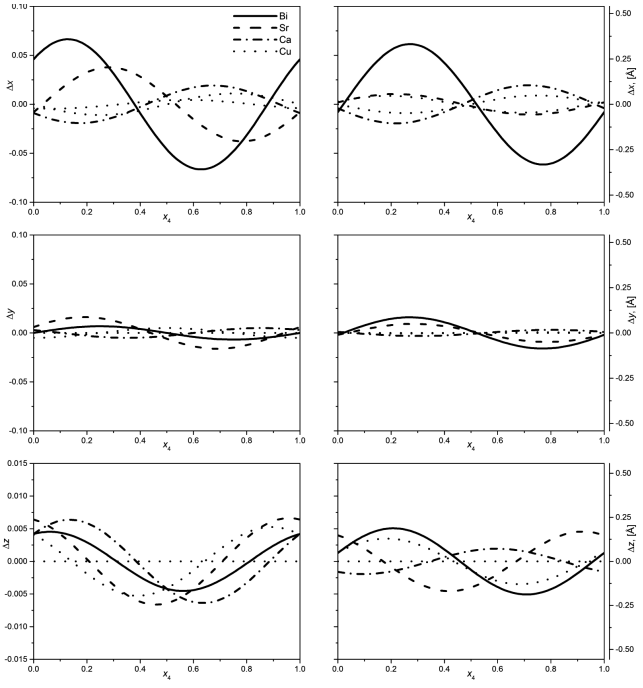

Fig. 2. Displacive modulation of the metal atom sites in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (left) and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ (right).

Refinements of the modulated structures were performed in the (3 + 1)D-superspace group $A2aa(\alpha 00)000$, considering up to 2nd order satellites corresponding to a modulation vector $\boldsymbol{q} = (0.2, 0, 0)$. Overall reliability factors of $R = 0.1434$ and 0.1383 ($wR = 0.1501$ and 0.1429) were achieved for $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$, respectively.

The crystal structure as refined in the average cell is presented in Fig. 1. The fractional atom coordinates, and isotropic and anisotropic displacement parameters are given in Table I and Table II (at the end). The displacive modulation parameters can be obtained from the authors upon request. The average structure was successfully used as starting model for the refinement of the modulated structure, without splitting of the Bi site.

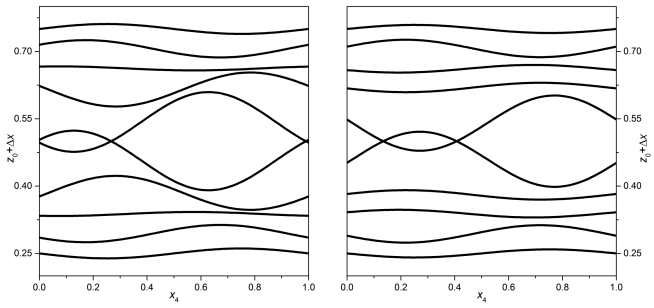

Fig. 3. Displacement of the metal atom sites along [1 0 0] in a structure block of $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (left) and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ (right).

TABLE I

Fractional atomic coordinates in $A2aa$ and isotropic or equivalent displacement parameters for $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ from a refinement in the (3+1)D-superspace group $A2aa(\alpha 00)000$.

Atom site		x	y	z	$U_{iso/eq}$ [Å^2]
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$					
Bi	8d	0.0	0.7290(2)	0.45758(3)	0.0547(3)*
Sr	8d	0.0128(7)	0.2459(5)	0.38523(8)	0.0632(8)*
Ca	8d	0.0370(7)	0.2501(6)	0.2951(1)	0.0576(12)*
Cu1	4c	0.0316(8)	3/4	1/4	0.0602(15)*
Cu2	8d	0.0111(6)	0.7494(5)	0.33851(8)	0.0544(12)*
O1	8d	0.278(3)	0.511(5)	0.1620(4)	0.024(51)
O2	8d	0.256(3)	0.005(4)	0.1653(4)	0.024(48)
O3	8d	0.284(2)	0.010(4)	0.2490(5)	0.024(44)
O4	8d	0.027(3)	0.414(5)	0.4542(5)	0.023(75)
O5	8d	-0.013(3)	0.259(3)	0.5906(5)	0.022(47)
$(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$					
Bi	8d	0.0	0.7280(1)	0.45762(2)	0.02513(17)*
Sr	8d	0.0233(4)	0.2479(3)	0.38561(5)	0.0306(5)*
Ca	8d	0.0320(5)	0.2496(4)	0.29388(7)	0.0209(6)*
Cu1	4c	0.0200(7)	3/4	1/4	0.0187(7)*
Cu2	8d	0.0138(5)	0.7501(3)	0.33828(6)	0.0186(5)*
O1	8d	0.265(3)	0.490(4)	0.1650(3)	0.015(53)
O2	8d	0.262(3)	0.008(4)	0.1634(3)	0.015(51)
O3	8d	0.267(3)	0.004(4)	0.2503(3)	0.014(47)
O4	8d	0.100(3)	0.339(4)	0.4564(5)	0.018(85)
O5	8d	0.019(4)	0.208(4)	0.6008(5)	0.011(92)

*$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

The corrugation of the atom layers and displacements of the atoms within the layers observed in the 3D commensurate approximant, were successfully described by modulation functions in (3+1)D superspace, using less parameters (Fig. 2). The inclusion of an additional oxy-

gen atom site inside the BiO layer, causing displacements of the Bi atoms within the layer, is the main origin of the modulation in the structure. The size misfit between the rocksalt- and perovskite-type slabs of the structure also leads to corrugation of the atom layers.

The displacements of the atoms along [1 0 0] induced in the BiO layer, decay while going towards the central square-planar CuO_2 layer (Fig. 3). The displacements of Bi atoms in neighboring layers are in phase, in contrast to what has previously been observed for members of the series Bi-2201 and Bi-2212, preserving high symmetry without any detectable monoclinic distortion.

4. Conclusions

A longitudinal displacement modulation, the magnitude of which increases from the CuO_2 to the BiO layers, was observed. The transverse displacement modulation showed the largest magnitude for the Cu and Ca atoms. Similar features were found for Pb-free and Pb-doped samples.

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TABLE II

Anisotropic displacement parameters (Å^2) for $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$

Atom site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$						
Bi	0.0486(5)	0.0537(4)	0.0619(8)	0.0014(4)	0.0033(5)	-0.0008(3)
Sr	0.0602(13)	0.0510(11)	0.0785(18)	0.0011(13)	0.0010(10)	0.0023(6)
Ca	0.0318(13)	0.0540(18)	0.087(3)	-0.0003(13)	0.0027(9)	0.0025(10)
Cu1	0.0357(16)	0.061(3)	0.084(3)	0	0	0.0018(9)
Cu2	0.0460(13)	0.0541(14)	0.063(3)	-0.0004(10)	0.0016(9)	0.0001(9)
$(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$						
Bi	0.0225(4)	0.0231(3)	0.0298(3)	-0.0013(3)	0.0020(3)	0.0001(1)
Sr	0.0243(8)	0.0247(8)	0.0428(9)	0.0015(5)	0.0010(5)	-0.0004(4)
Ca	0.0033(9)	0.0179(10)	0.0415(14)	-0.0001(4)	0.0011(5)	-0.0005(5)
Cu1	0.0015(10)	0.0062(10)	0.0484(14)	0	0	-0.0003(5)
Cu2	0.0048(8)	0.0108(8)	0.0401(11)	0.0008(6)	-0.0018(6)	0.0000(4)