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X-ray analysis of the incommensurate modulation in the 2:2:1:2 Bi-Sr-Ca-Cu-O superconductor including the oxygen atoms

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Single-crystal x-ray diffraction data on the 2:2:1:2 Bi-Sr-Ca-Cu-O superconducting phase have been used in a four-dimensional refinement of the modulations of both the metal and oxygen atoms. An expression for an analytical temperature-factor modulation function has been derived and applied to the bismuth atoms. The large value of the temperature factor of Bi in some of the unit cells indicates a contribution from static disorder. The modulation of the oxygen atoms in the bismuth layer is best described by a function that allows the displacement to vary linearly with unit-cell position and incorporates the possibility of excess oxygen near the end of a modulation period. The results on oxygen occupancy and the behavior of the Bi temperature factor are compatible with models that attribute the origin of the modulation to the existence of extra oxygen atoms in the Bi-O layers. Refinement in the noncentrosymmetric super space group $M{:}A2aa{:}\bar{1}11$ leads to significantly better results than the centrosymmetric treatment.

I. INTRODUCTION

In an earlier report,[1] we have described the modulation in the 2:2:1:2 Bi-Sr-Ca-Cu-O superconductor as determined from the refinement of the main and first-order satellite reflections. The model was based on the centrosymmetric super-space group $M{:}Amaa{:}\bar{1}11$.[2] The results of the analysis indicate large amplitude modulational displacements of the Bi and Sr atoms in the **a** and **c** directions and of the Cu atoms in the **c** direction only.

As the modulation of oxygen atoms were not refined, the description of the modulation was necessarily incomplete. In the present study, which includes the second-order satellite reflections, several modifications in the refinement procedure were made, and the modulation of the weakly scattering oxygen atoms was included.

The first modification is related to the observation, from four-dimensional difference Fourier maps, that the modulation of the Bi atoms cannot be fully described as a positional modulation. The four-dimensional maps, in which all positions of Bi in the crystal are represented, show large maxima on both sides of the Bi positions at certain values of the internal (fourth-dimension) coordinate t. This indicates either a positional disorder, or a larger atomic vibration in some of the unit cells. The effect can be described by the introduction of a four-dimensional temperature factor in the refinement.

A second change concerns the choice of superspace group. Bordet *et al.*[3] have interpreted their neutron-diffraction power data in terms of the noncentrosymmetric space group $A2aa$. This choice allows more reasonable oxygen positions and improves the coordination of the Bi atom. A further indication of a possible lowering of the symmetry is the electron-diffraction observation of Eibl[4] of a number of reflections violating the A-centering of the unit cell.

Our recent study of the Bi distribution in the crystal using anomalous scattering synchrotron techniques,[5] indicates partial Bi occupancy of the Sr and Sr/Ca layers. The experimental occupancies from the study were introduced in the final stages of the refinement, which included in addition to the earlier data the newly collected second-order satellite reflections.

II. EXPERIMENTAL

The single crystal used in the present study was obtained from M. A. Subramanian at the Dupont Central Research Station and has dimensions of $0.05\times0.17\times0.008$ mm^3. Cell dimensions and the **q** vector were determined from the positions of a number of high-order main and satellite reflections as $a=5.408(1)$ Å, $b=5.413(1)$ Å, $c=30.871(5)$ Å, $\alpha=\beta=\gamma=90°$, and $\mathbf{q}=0.210(3)\mathbf{a}^*$. A total number of 1844 reflections with $\theta<35°$ were measured on a CAD4 automated diffractometer with $MoK\alpha$ radiation ($\lambda=0.7101$ Å), and averaged to give 658 unique reflections with $I>3\sigma(I)$—including 108 first and 61 second order satellites. Only two relatively weak and diffuse reflections violating the A centering were observed, thus confirming the symmetry of the translation lattice.

A parallel refinement was performed on a second crystal obtained from Dr. Zhao at the Academica Sinica in Beijing. As the results of the second crystal were essentially identical to those obtained on the first specimen, only the refinement of the first crystal are discussed here.

III. LEAST-SQUARES REFINEMENT AND (3+1) DIMENSIONAL FOURIER-SYNTHESES

The refinement was performed in several stages. R factors, defined by ($R = \sum_{\text{refl}} ||F_c| - |F_0|| / \sum_{\text{refl}} |F_0|$), where the summations are over all observed reflections, are given in the form ($R|R^{(0)}$, $R^{(1)}$ $R^{(2)}$), where $R, R^{(0)}$, $R^{(1)}$, and $R^{(2)}$ are R values for all reflections, main reflections, first-order satellites, and second-order satellites, respectively.

A. Modulation of Bi atoms

The result of Ref. 1 was used as a starting point of the refinement. The Ca/Sr layer at $z=0.5$, which was kept at the average positions in the previous work, was included in the modulation refinement. The occupancies were fixed at their ideal values in the refinement, which led to $R=(12.7|11.0,11.7,49.3)$. The subsequent four-dimensional Fourier maps show large maxima and minima in the BiO layer. As the modulation of the Bi atom has a large component along the **a** direction the effect can be illustrated in a two-dimensional t-x section containing the average Bi position (Fig. 1). The modulated position of the Bi atom is drawn in Fig. 1 as a dashed line. The difference densities [Fig. 1(b)] are quite different for $t \sim 0$ and $t \sim 0.4$ or 0.6. For $t \sim 0$ the Bi atom is located in a deep minimum surrounded (for constant t) by local maxima, while for $t \sim 0.4$ and 0.6 the atom is at a large maximum surrounded by local minima. Such an effect, whether static or dynamic, can be described in terms of a four-dimensional temperature parameter.[6] An analytical description of the temperature factor modulation, described in Appendix A, was introduced in the refinement program JANA.[7] Inclusion of first- and second-order harmonic terms for the Bi temperature factor modulation led to a considerable improvement in agreement factors: $R=(10.0|9.0$, 10.4, and 26.4).

The modulation is especially significant for U_{11} for which the expression $U_{11}=0.066+0.064\cos(2\pi x_4)+0.053\cos(4\pi x_4)$ (in Å^2) was obtained. This equation leads to $(U_{11})_{\max}=0.183$ Å^2 (for $x_4=0.0$) and $(U_{11})_{\min}=0.003$ Å^2 (for $x_4=0.3$ and 0.7). The large size of the fluctuation suggests a static disorder in the Bi position.

B. Treatment of the oxygen modulation

With the much better fit obtained in the previous refinements, a four-dimensional difference map was calculated, omitting from the calculations only the O(3) and O(4) oxygen atoms, which coordinate the Bi atom. Figure 2 shows the two most important sections of these maps. The very large positional modulation of the oxygen atoms along the a direction is evident. In Fig. 2(b) the O(4) atom appears as a diagonal ridge in the t-x plane. This strongly suggests that a linear variation of the magnitude of the displacement will describe the modulation of the oxygen atoms better than the harmonic function, which corresponds to a sinusoidal shaped string in the t-x plane (as observed for Bi in Fig. 1a). Such a linear function of which the slope and length are variable parameters (Appendix B) was therefore introduced in the refinement. The resulting values of R (8.4 |7.8, 7.7, 24.6) are slightly better than those obtained with a harmonic model for the oxygen modulation $\{R=(8.5|8.0,7.4,25.3)\}$, even though the number of parameters for the modulation of O(4) was reduced from six to four (i.e., the three components of u_0 and the parameter Δ—Fig. 3).

The modulation function is such that the x coordinate of O(4) changes abruptly between the fourth and the fifth unit cell along the a axis. This effect is also visible in Fig. 2(b) in which the O atom has two positions for $t=0$ (at the bottom and the top of the map) at $x=+0.15$ and $x=-0.15$. This is also the region where the Bi atom has a very large apparent thermal motion, indicating a local distortion of the structure.

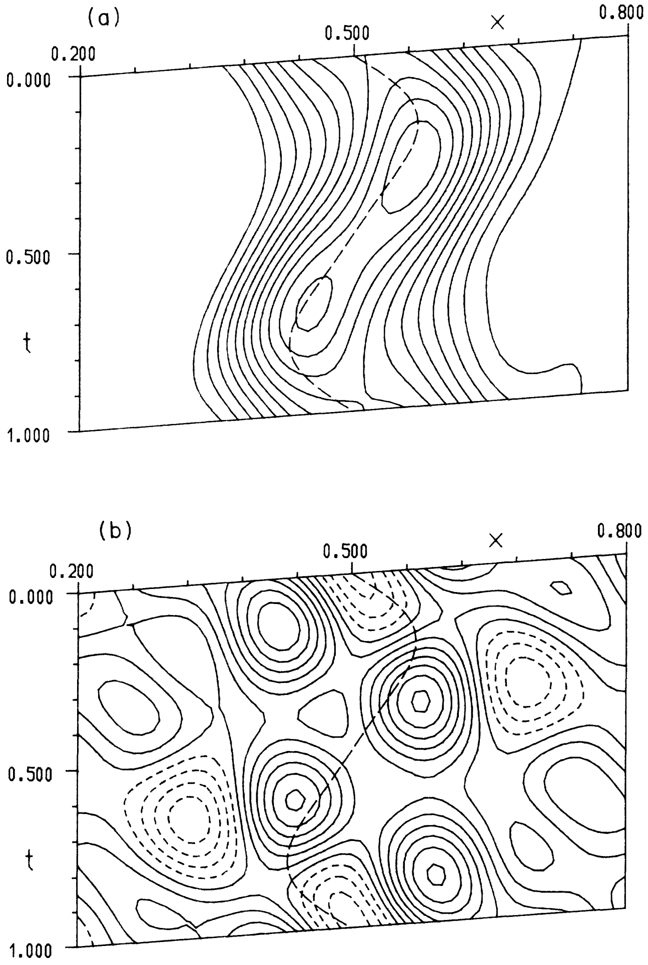

FIG. 1. The modulated Bi atom: (a) The section x-t($y=0.228$, $z=0.052$) of the four-dimensional Fourier map. Contours at intervals of 20e Å^{-3} and (b) the same section in the four-dimensional difference map. Contours at 2e Å^{-3}. The string representing the modulated Bi is drawn as a dashed line. Negative contours are broken.

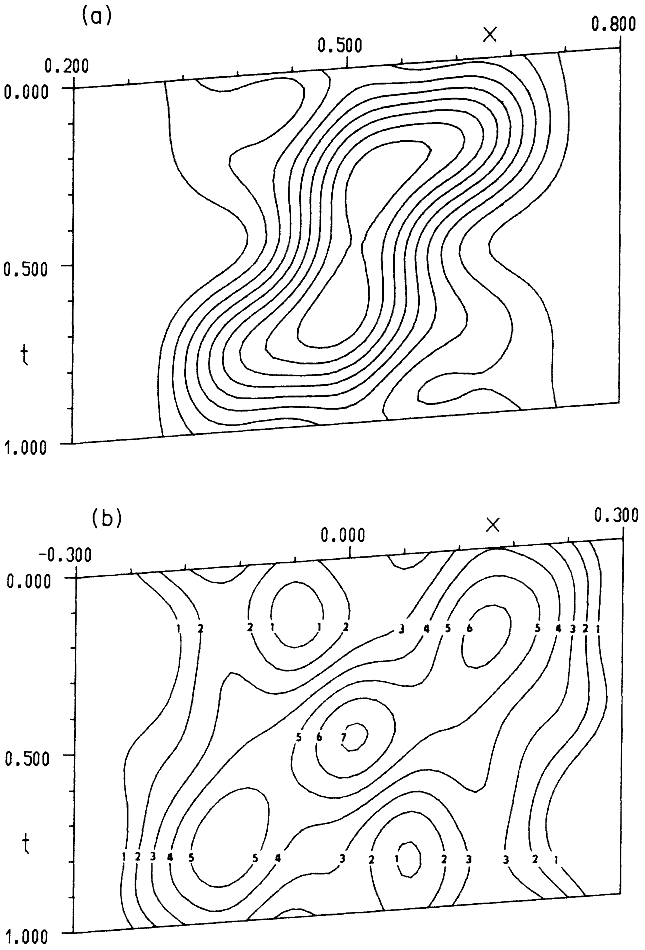

FIG. 2. *x*-*t* sections of the four-dimensional difference Fourier map, calculated after the refinement of the modulation of temperature parameters of the Bi atom showing the modulation of the oxygen atoms O(3) and O(4): (a) the O(3) atom (section at $y=0.279$, $z=0.121$); (b) the O(4) atom (section at $y=0.146$, $z=0.054$). Contours at intervals of 1e Å^{-3}.

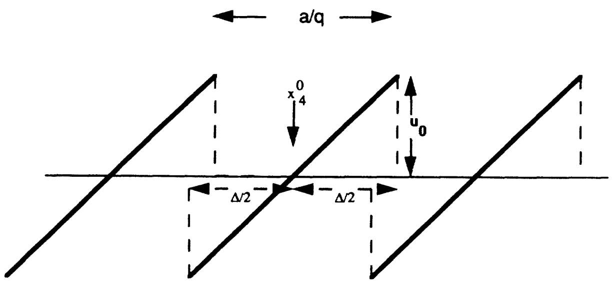

FIG. 3. The oxygen modulation model: displacement (vertical axis) vs unit-cell position along the **a** axis (horizontal axis).

C. Noncentrosymmetric refinement

In the next stage the refinement was continued, using the noncentrosymmetric superspace group $M:A2aa:\bar{1}11$. As the number of observed reflections is too small to refine the parameters of all atoms, and deviations from the centrosymmetric structure are most likely in the BiO layers, only the atoms Bi, O(3), and O(4) were allowed to deviate from the centrosymmetric arrangement. The final values are considerably better than those of the centrosymmetric refinement: $R=(7.2|7.0,\ 6.5,\ 16.1)$ and $R=(8.1|7.6,\ 7.9,\ 14.7)$ for the two crystals respectively. The resulting atomic parameters are summarized in Tables I and II.

The occupancy of the extra oxygen is given by Δ-1, where Δ is the adjustable parameter in the oxygen modulation model (Appendix B). Δ values for the two crystals are 1.04(7) and 1.12(5), corresponding to the chemical formula $Bi_2Sr_2CaCu_2O_{8.1}$ and $Bi_2Sr_2CaCu_2O_{8.2}$, respectively.

Since a synchrotron anomalous scattering experiment gave evidence for Bi occupancy of the Sr and Sr/Ca layers,[4] a final refinement was performed using the synchrotron-determined Bi occupancies.

D. Cation occupancies

The occupancies of the Bi, Sr, and Sr/Ca sites were refined, keeping the Bi occupancies of the last two sites fixed at the values from the synchrotron experiment. The refined values differ from the earlier results because of the refinement modifications described previously. Results for crystal 1 are listed in Table III. The R factors of this refinement are identical to those obtained in the previous step, indicating the lack of sensitivity of the conventional x-ray results to details of the site occupancy.

The most significant difference with the earlier results[4,8] is the occupancy of the BiO layer which is fully occupied according to the refinement. However, as will

TABLE I. Positional and thermal parameters (Å × 10^3) of the average structure.

	x	y	z	$U(1,1)/U(\text{iso})$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Bi	0.505(2)	0.2327(5)	0.0523(9)	71(3)	21(2)	13(2)	−8(4)	10(4)	−4(2)
Sr	0	0.2525(5)	0.1408(1)	23(2)	5(2)	21(2)	0	0	5(3)
Cu	0.500	0.2499(6)	0.1965(1)	10(2)	−1(3)	23(3)	0	0	−4(4)
Ca	0	0.250	0.2500	9(3)	5(3)	21(5)	0	0	−2(7)
O(1)	0.75	0	0.197(1)	10					
O(2)	0.25	0.50	0.199(1)	10					
O(3)	0.53(2)	0.289(6)	0.116(1)	10					
O(4)	0.02(2)	0.157(5)	0.056(2)	10					

TABLE II. Amplitudes (Å) of the positional and thermal parameter (Å × 10^3) modulations.

	Wave	U_x	U_y	U_z	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Bi	$\sin(2\pi x_4)$	0.33(1)	0.06(1)	−0.01(1)	−33(4)	25(4)	4(5)	−8(3)	−2(2)	−4(5)
	$\cos(2\pi x_4)$	0.08(2)	−0.04(1)	−0.16(1)	51(6)	1(4)	−5(2)	19(6)	6(5)	−7(3)
	$\sin(4\pi x_4)$	0.09(1)	0.01(2)	−0.06(1)	−14(9)	5(6)	1(5)	21(6)	28(3)	−30(3)
	$\cos(4\pi x_4)$	−0.01(2)	−0.11(1)	−0.06(1)	54(4)	−14(4)	−8(4)	21(6)	−5(6)	−1(6)
Sr	$\sin(2\pi x_4)$	0.22(1)	0	0						
	$\cos(2\pi x_4)$	0	0.04(3)	−0.21(1)						
	$\sin(4\pi x_4)$	0.10(1)	0	0						
	$\cos(4\pi x_4)$	0	0.02(4)	−0.07(2)						
Cu	$\sin(2\pi x_4)$	0.06(6)	0	0						
	$\cos(2\pi x_4)$	0	−0.03(2)	−0.28(1)						
	$\sin(4\pi x_4)$	−0.01(1)	0	0						
	$\cos(4\pi x_4)$	0	0.08(3)	−0.07(1)						
Ca	$\sin(2\pi x_4)$	0	0	0						
	$\cos(2\pi x_4)$	0	−0.01(5)	−0.26(1)						
	$\sin(4\pi x_4)$	−0.04(2)	0	0						
	$\cos(4\pi x_4)$	0	0	0						
O(1)	$\sin(2\pi x_4)$	0.06(9)	0.06(16)	0						
	$\cos(2\pi x_4)$	0	0	−0.39(7)						
	$\sin(4\pi x_4)$	−0.08(7)	0.01(12)	0						
	$\cos(4\pi x_4)$	0	0	−0.08(9)						
O(2)	$\sin(2\pi x_4)$	0.03(8)	−0.05(15)	0						
	$\cos(2\pi x_4)$	0	0	−0.11(9)						
	$\sin(4\pi x_4)$	0.06(7)	−0.04(11)	0						
	$\cos(4\pi x_4)$	0	0	0.27(7)						
O(3)	$\sin(2\pi x_4)$	0.45(6)	0.03(16)	0.05(11)						
	$\cos(2\pi x_4)$	0.23(11)	0.08(6)	−0.32(6)						
	$\sin(4\pi x_4)$	0.29(7)	0.02(14)	−0.15(13)						
	$\cos(4\pi x_4)$	0.11(12)	0.13(8)	−0.23(8)						
O(4)	$\mathbf{u}_0$ (Å)	−1.59(10)	0.08(8)	0.53(7)						
	x_4^0, Δ[a]	0.44(4)	1.04(8)							

[a] In fractional coordinates, as defined in Appendix B.

be discussed subsequently the large temperature factor of the Bi atom with $x_4 = 0$ may indicate a Bi deficiency in this region. The final chemical formula is $Bi_{2.15}Sr_{1.92}Ca_{0.75}Cu_2O_{8.1}$ corresponding to a value of 2.21(4) for the valency of the Cu atom. A deficiency of Bi in the BiO layer would increase this value.

IV. DISCUSSION

As described in the earlier report, the **a**-axis displacements of Bi atoms in adjacent layers are in phase, while the **c**-axis displacements are such that adjacent atoms in the two layers move away from or towards each other.[1,8] This is in agreement with electron micrographs observations made in several laboratories,[9] and is a feature preserved for the $\mathbf{q}_1$, but not the $\mathbf{q}_2$ modulation in the lead-doped 2:2:1 phase.[10]

The occurrence of extra oxygen atoms as a possible reason for the existence of the modulation was proposed by Zandbergen *et al.*[11] based on electron transmission microscopy data, and by LePage[12] *et al.* based on the analysis of the commensurate Fe and Mn analogs of the Bi cuprates. The positions of the Bi and O(4) atoms in five successive unit cells of the BiO layer are shown in

TABLE III. Site occupancies from the least-squares refinement.

	From Ref. 5[a]	From Ref. 8[b]	This work
Bi/Bi	0.874	0.93	0.99(2)
Bi/Sr	0.05	0.05	0.05
Sr/Sr	0.79(3)	0.84(3)	0.86(2)
Bi/Ca	0.06	0.06	0.06
Sr/Ca	0.14(8)	0.17(7)	0.19(5)
Ca/Ca	0.80	0.77	0.75

[a] Excluding the modulation of the Ca layer.

[b] With modulation of the Ca layer.

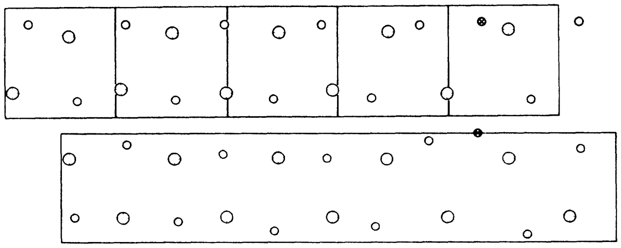

FIG. 4. The distribution of bismuth and oxygen atoms in the BiO layer. Top–according to the present study. Lower–as derived by LePage *et al.* (Ref. 12) for the fivefold cell of the commensurate analog $Bi_{10}Sr_{15}Fe_{10}O_{46}$. ○ denotes bismuth; ○ denotes oxygen, and ⊗ denotes extra oxygen.

Fig. 4. The agreement with the results of LePage *et al.* is very good—the main difference being the smaller displacement of O(4) in the **b**-axis direction. The region near the boundary between the fourth and the fifth cell contains extra oxygen, but is highly distorted as indicated by the large value of the four-dimensional Bi temperature parameter in this region. There is a striking correspondence with the Scanning Tunneling Microscopy study of Kirk *et al.* which shows a missing row of bismuth atoms for every 9.6 bismuth atoms (4.8 unit cells) in the **a** direction.[13] If the surface and bulk structure are similar, which Kirk *et al.* argue is likely,[13] the large Bi temperature factor can be interpreted as indicating an empty Bi site in the crystal, which is at least partly filled by extra oxygen atoms not observable by STM. However, there is no clear evidence for this interpretation in the four-dimensional Fourier maps shown in Fig. 1.

Though the oxygen modulations cannot be determined with great accuracy in this x-ray study, it is clear that the displacements are not confined to the rock salt part of the structure. Both the Cu and the O atoms of the CuO_2 layers undergo large modulations, which represent a variation of the geometry of the Cu-O-Cu linkage along the **a**-axis direction. That the modulation has a significant effect on the band structure of the solid has been demonstrated in a recent calculation[14] using the distortions as determined from the commensurate analogues of the Bi cuprates.[12]

In summary, our results are fully compatible with the existence of extra oxygen in the BiO layers. Whether the extra oxygen or the size mismatch between the rock salt and perovskite parts of the structure is the origin of the modulation[15,16] remains a subject for further discussion.

ACKNOWLEDGMENTS

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APPENDIX A

Let us consider that the positional modulation as defined in (7) by Eq. (1) is accompanied by the modulation of the mean-square displacement tensors:

$$\beta_{n\nu}=\beta_\nu^0+\beta_\nu[\mathbf{q}_1\cdot(\mathbf{g}_\nu+\mathbf{n}),\ldots,\mathbf{q}_d\cdot(\mathbf{g}_\nu+\mathbf{n})]\ , \tag{A1}$$

where $\beta_{n\nu}$ and β_ν^0 are the tensor of the temperature parameters in the nth cell, and the average temperature parameter tensor of atom ν, respectively. **g** is the phase reference point, which is equal to the atomic position for an atom not part of a rigidly displaced entity. β_ν is the d-dimensional periodic tensor function

$$\beta_\nu(x_1,\ldots,x_d)=\beta_\nu(x_1+n_1,\ldots,x_d+n_d)\ ,$$

($n_1,\ldots,n_d$ being integers).

Similarly, as for $\mathbf{u}_\nu$ [see expression 2 in Eq. (7)], we can write

$$\begin{aligned}\beta_\nu=&\sum_{i=1}^{l}\beta_\nu^x(i)\sin[2\pi\mathbf{q}_i\cdot(\mathbf{n}+\mathbf{g}_\nu)]\\&+\sum_{i=1}^{l}\beta_\nu^y(i)\cos[2\pi\mathbf{q}_\mathrm{i}\cdot(\mathbf{n}+\mathbf{g}_\nu)]\ ,\end{aligned} \tag{A2}$$

where the summation is over all distortion waves, including higher harmonic terms. Analogous to Eq. (7) we introduce the amplitude $\beta_\nu(i)$ and phase $\eta_\nu(i)$, such that

$$\begin{aligned}&\beta_\nu(i)=\{[\mathbf{h}^T\beta_\nu^x(i)\mathbf{h}]^2+[\mathbf{h}^T\beta_\nu^y(i)\mathbf{h}]^2\}^{1/2}\ ,\\&\sin\eta_\nu(i)=\mathbf{h}^T\beta_\nu^y(i)\mathbf{h}/\beta_\nu(i)\ ,\\&\cos\eta_\nu(i)=\mathbf{h}^T\beta_\nu^x(i)\mathbf{h}/\beta_\nu(i)\ .\end{aligned} \tag{A3}$$

With the Jacobi-Auger expansion

$$\begin{aligned}\exp(-z\sin\alpha)=&\sum_m J_{-m}(iz)\exp(-im\,\alpha)\\=&\sum_m I_{-m}(z)\exp[-im\,(\alpha+\pi/2)]\ ,\end{aligned} \tag{A4}$$

where I_m is the modified Bessel function $I_m(z)=i^{-m}J_m(iz)$, one obtains for the contribution of the υth atom to the structure factor F, after summation over all symmetry-related atoms N_S

$$\begin{aligned}F_\nu(\mathbf{Q})=&\sum_{j=1}^{N_S}f_\nu(\mathbf{Q})\exp(2\pi i\mathbf{Q}\mathbf{r}_{E\nu}^j)\exp(-2\pi i\mathbf{M}\Gamma_I^j\sigma\mathbf{g}_{E\nu})\exp[-2\pi i\mathbf{M}(\sigma\mathbf{s}_E^j-\mathbf{s}_I^j)]\exp(-2\pi i\mathbf{h}^\mathrm{T}\beta_\nu^{0j}\mathbf{h})\\&\times\sum_{\substack{m_1\ldots m_l\\ [(\mathbf{m}+\mathbf{n})\alpha=\mathbf{M}\Gamma_E^j]}}^{+\infty}\ \sum_{n_1\ldots n_1=-\infty}^{+\infty}\prod_{i=1}^{l}\{J_{-m}[2\pi U_\nu^j(i)]\exp[-im_i\chi_\nu^j(i)]\}\prod_{i=1}^{l}\{I_{-n}[\beta_\nu^j(i)]\exp[-in_i(\eta_\nu^j(i)+\pi/2)]\}\ ,\end{aligned} \tag{A5}$$

where the superscript j for $\beta_\nu^j(i)$ and $\eta_\nu^j(i)$ indicates the use of symmetry-related amplitudes (A3) of the modulation of temperature parameters. Other symbols are as defined in Ref. 7: Γ and $\mathbf{s}$ are the rotational and translational elements of the multidimensional symmetry operator such that $\mathbf{r}_{E\nu}^j=\Gamma_E^j \mathbf{r}_{E\nu}+\mathbf{s}_E^j$, $\mathbf{M}$ and σ are the satellite indices and the components of the $\mathbf{q}$ vector, respectively, and the subscripts E and I indicate external and internal coordinates.

APPENDIX B

The four-dimensional Fourier map [Fig. 2(b)] suggests that the positional modulation function of the O(4) atom can be described by a linear "sawtooth" function

$$\mathbf{u}=2\mathbf{u}_0[(x_4-x_4^0)/\Delta] \text{ for } (x_4^0-\Delta/2<x_4<x_4^0+\Delta/2)\ , \tag{A6}$$

an empty position outside this range if $\Delta<1$. Values of $\Delta>1$ lead to two atoms $2\mathbf{u}_0$ apart in cells for which the coordinate x_4 is in the range $(x_4^0+\Delta/2, x_4^0-\Delta/2+1)$, as illustrated in Fig. 3. The quantity $\Delta-1$ is the occupancy of this extra position.

The one-dimensional Fourier transform of the modulation function (A6) leads to

$$L_m(\Delta,\alpha,x_4^0)=\exp(2\pi i m x_4^0)\Delta\sin(\pi m\Delta+\alpha)/(\pi m\Delta+\alpha)\ , \tag{A7}$$

where $\alpha=2\pi\mathbf{h}\mathbf{u}_0$. This function can be used instead of the Bessel function J_m in the formula (A5).

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