DIMS (Direct-method program of solving Incommensurate Modulated Structures)/VEC applications

Hai-fu Fan
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, P. R. China
E-mail: fan@mail.iphy.ac.cn ; WWW: http://cryst.iphy.ac.cn/

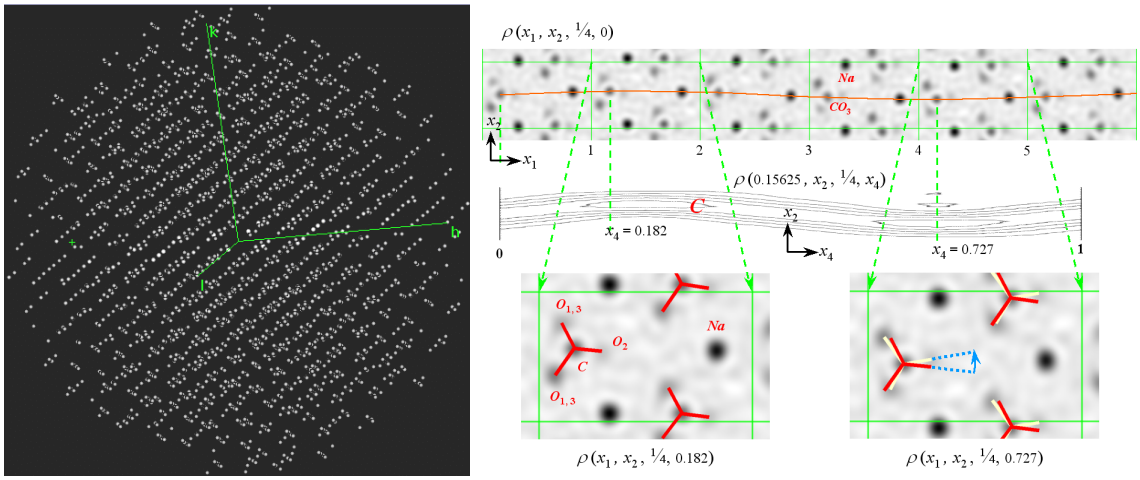
(Editors' note: the referred to files are included as an Zipped addendum package at the Comp Comm Newsletter No 5 website)

1. Introduction

The integration of DIMS (Fu et al., 1994, 1997; Li et al., 1999) and VEC (Wan et al., 2003) provides an intuitive and automatic way of solving incommensurate structures. Calculations are visually performed on the VEC platform mostly via mouse clicks. Examples are given here involving two incommensurate modulated structures and the 4-dimensional basic structure of a composite crystal. As will be seen, structural details including the incommensurate modulation can be observed objectively prior to the model building and least-squares refinement. For detailed operations of the program DIMS/VEC the reader is referred to the paper "DIMS on the VEC platform" in this newsletter.

2. Direct observation of the incommensurate modulation of γ-Na_2CO_3

Crystals of γ-Na_2CO_3 have a one-dimensionally modulated incommensurate structure with unit cell parameters of the basic structure $a = 8.904$, $b = 5.239$, $c = 6.042$Å, $\beta = 101.35^o$ and the modulation wave vector $\boldsymbol{q} = 0.182\boldsymbol{a}^* + 0.318\boldsymbol{c}^*$. The superspace group is P[C 2/m] –1 s (two-line symbol used in DIMS). Van Aalst et al. (1976) originally solved the modulated structure by trial-and-error method. Hao et al. (1987) used their data to test the multidimensional direct method. 300 largest main reflections, 250 largest first order satellites and 150 largest second order satellites from the experimental data were selected for the test. The program SAPI (Yao et al., 1985) was used to derive phases of main reflections, based on which the multidimensional direct method was used to phase satellite reflections. There is no need to know the basic structure in advance. In the present test, the input file **Na2CO3.key** was constructed with the same data used by Hao et al. (1987). The output file **Na2CO3.hklm** was produced and opened in a sub-window on the VEC platform (see Fig. 1). The file contains the original input data together with the direct-method phases of satellite reflections. Fig. 2 shows sections of the 4-dimensional electron density map of γ-Na_2CO_3 calculated with the file **Na2CO3.hklm**. The top row of Fig. 2 shows the half-tone graphic section of the 4-dimensional electron-density map at x_3 (z) = ¼. Six unit cells are plotted along the $\boldsymbol{x}_1$ axis. Since the modulation wave vector $\boldsymbol{q}$ has a component $q_1 = 0.182$ along $\boldsymbol{a}^*$, the modulation period should be about 5.5 unit cells along the $\boldsymbol{x}_1$ axis. Consequently the first unit cell on the left of the top row corresponds to $x_4 = 0.0$, while the sixth unit cell corresponds to $x_4 \approx 1.0$. This is evident comparing the top row and the middle row, the contoured section ρ (0.15625, x_2, ¼, x_4). As is seen the top section reveals clearly sodium atoms and CO_3 groups. It is seen also that the x_2 coordinate of carbon atoms varies along the $\boldsymbol{x}_1$ axis from one unit cell to the other indicating the positional modulation of the carbon atoms as shown by the red curve. This can be seen more precisely on the section ρ (0.15625, x_2, ¼, x_4). By comparing the second and the fifth unit cell (see the bottom row of Fig. 2), it is observed that the modulation of the CO_3 groups performs an anticlockwise rotation around the axis through the carbon atom perpendicular to the ($\boldsymbol{a}$, $\boldsymbol{b}$) plane ($\boldsymbol{a}$ and $\boldsymbol{b}$ are respectively the projection of $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ along the direction perpendicular to the 3-dimensional physical space). All these features are consistent with the original result of Van Aalst et al. (1976). One of the most important differences between DIMS/VEC and the trial-and-error method is that all features of the structural modulation of γ-Na_2CO_3 are visualized on the direct-method phased electron-density map, which does not rely on any assumptions concerning the form of modulation waves and is obtainable prior to model building and structure refinement.



Figures 1 (left) and 2 (right)

3. Visualizing structural modulation of Bi-2212

The incommensurate structure of the high-Tc superconductor $Bi_2Sr_2CaCu_2O_y$ (Bi-2212) has been extensively studied in a number of laboratories over the world. However the results are not completely consistent with each other. Here DIMS/VEC produces the visualized structural modulation without relying on any assumptions on the modulation waves. The data used in this test is the same as that of Fu et al. (1995). Crystals of Bi-2212 belong to the superspace group N[Bbmb]1-11 (two-line symbol used in DIMS) with unit cell parameters of the basic structure $a = 5.422$, $b = 5.437$, $c = 30.537$Å and the modulation wave vector $\boldsymbol{q} = 0.22\boldsymbol{b}^* + \boldsymbol{c}^*$. SAPI was used to derive phases of the main reflections.

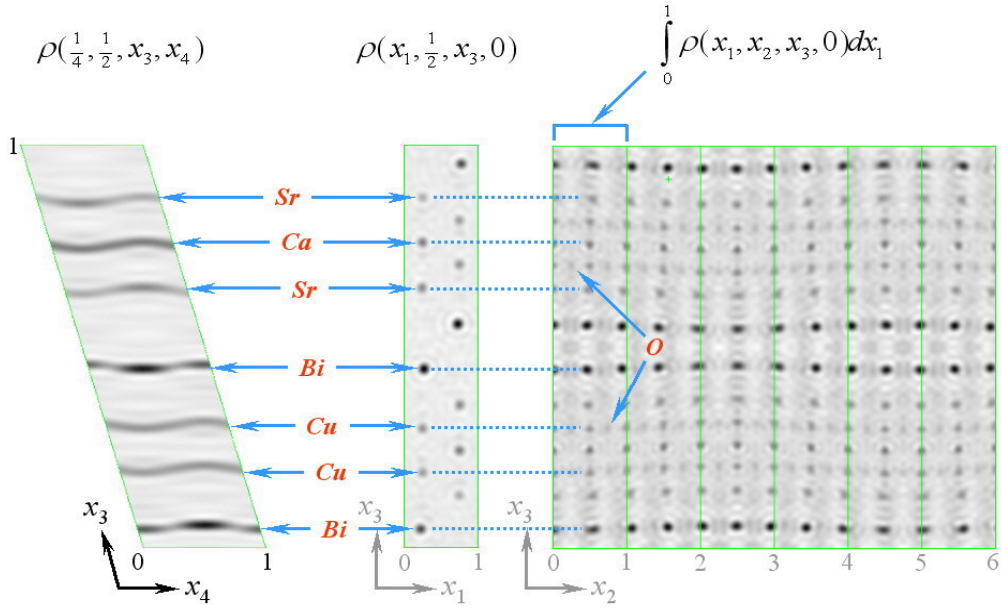


Figure 3:

Fourier recycling was used to determine the basic structure. The input file **Bi-2212.key** was then constructed, with which DIMS/VEC produced the output file **Bi-2212.hklm**. Electron-density maps were calculated on the VEC platform. The 4-dimensional electron-density function of Bi-2212 projected along the $\boldsymbol{x_1}$ axis is shown on the right of Fig. 3 giving an overview of the incommensurate structure. Six unit cells are plotted along the $\boldsymbol{x_2}$ axis. All metal atoms and the oxygen atoms on Cu-O layers are clearly seen. The section at $x_2 = ½$, $x_4 = 0$ shown in the middle of Fig. 3 contains all the independent metal atoms.

Their modulation is shown on the section ρ (¼, ½, x_3, x_4) (on the left of Fig. 3). Fig. 4 shows atoms on the Cu-O layer and the modulation of the oxygen atom O(1). Fig. 5 shows the saw-tooth modulation of the oxygen atom O(4). It should be emphasized that the saw-tooth modulation here is not a result of least-squares refinement based on a guessed model. In contrast it is revealed objectively before any efforts of model building.

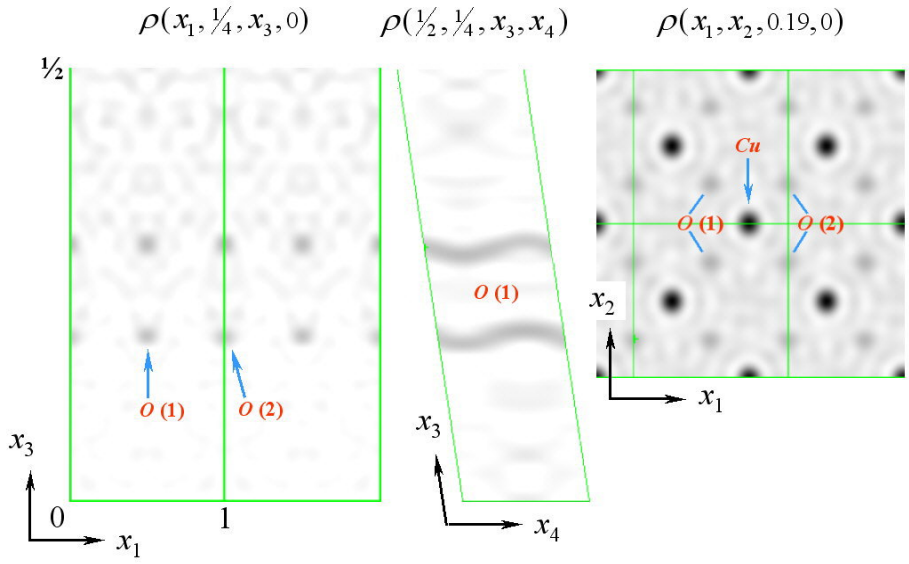


Figure 4:

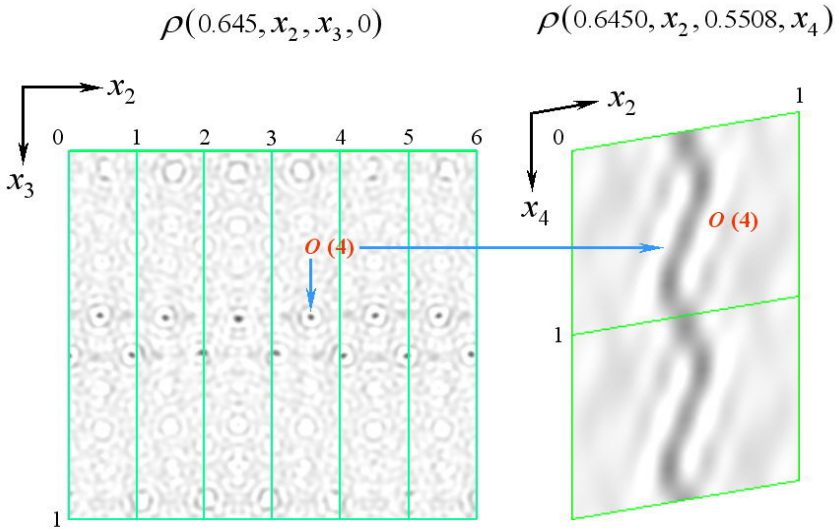
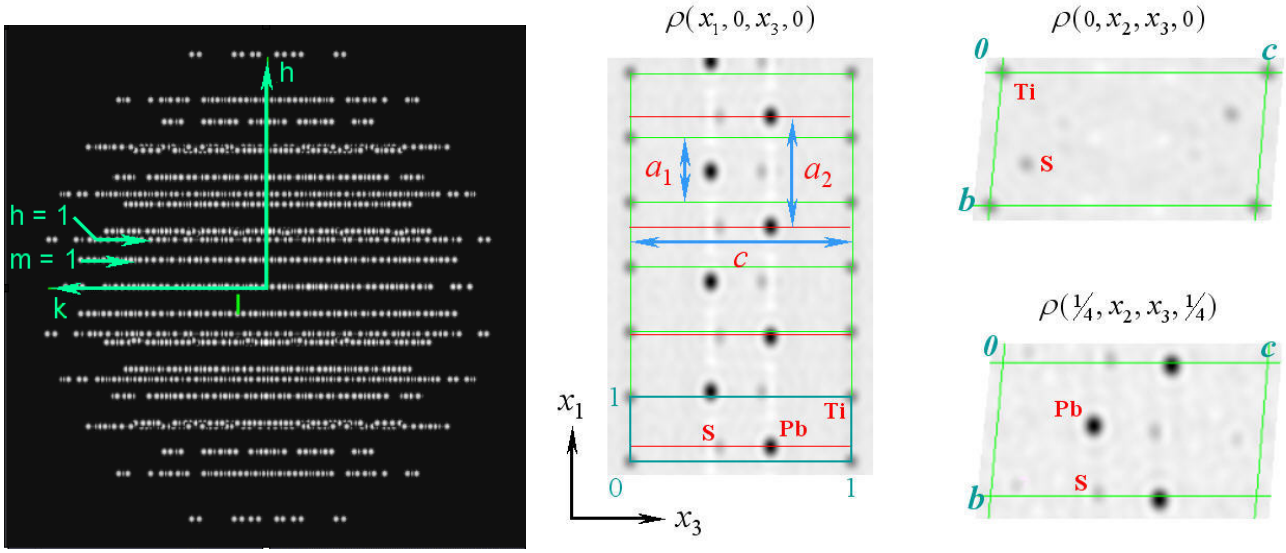


Figure 5:

4. Solving the 4-dimensional basic structure of the composite crystal $(PbS)_{1.18}TiS_2$

The composite structure of $(PbS)_{1.18}TiS_2$ (Van Smaalen et al., 1991) belongs to the space group C2/m (α, 0, 0) s-1. It consists of two subsystems: the subsystem TiS_2 with $a_1 = 3.409$, $b_1 = 5.880$, $c_1 = 11.760$Å $\alpha_1 = 95.29^o$ and the subsystem PbS with $a_2 = 5.800$, $b_2 = 5.881$ $c_2 = 11.759$Å, $\alpha_2 = 95.27^o$. Within the experimental error we have $b_1 = b_2$, $c_1 = c_2$, and $\alpha_1 = \alpha_2$. Unlike conventional incommensurate modulated structures, there are no 3-dimensional basic structures corresponding to a composite structure. For $(PbS)_{1.18}TiS_2$, the basic structure is a 4-dimensional one. It is more complicated to determine such a basic structure than to fine the modulation of $(PbS)_{1.18}TiS_2$, since there are no known phases available for

the direct-method phasing except the origin and enantiomorph fixing ones. The following test shows that DIMS/VEC is capable of solving the 4-dimensional basic structure in a straightforward manner. The input file **PbTiS.key** contains only main reflections. The symmetry is assumed to be non-centrosymmetric. The output file from DIMS/VEC is **PbTiS.hklm**, which is opened in a sub-window as shown in Fig. 6. Sections of the 4-dimensional electron-density maps calculated from **PbTiS.hklm** are shown below. On the left of Fig. 7 we see the "chimney and ladder" structure along the $\boldsymbol{x}_1$ axis constructed by the TiS_2 subsystem with the period a_1 and the PbS subsystem with the period a_2. On the right of Fig. 7 there are sections through the TiS_2 layer and PbS layer parallel to the (***b***, ***c***) plane. Note that $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, ***b*** and ***c*** are respectively the projection of the axes $\boldsymbol{x}_1$, $\boldsymbol{x}_4$, $\boldsymbol{x}_2$ and $\boldsymbol{x}_3$ along the direction perpendicular to the 3-dimensional physical space. Again all the structural features are visible on the direct-method phased electron-density map before any efforts of model building and structure refinement.



Figures 6 (left) and 7 (right)

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