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Dynamical Diffraction Calculations of Incommensurate Modulations in Crystals

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Quantitative electron diffraction (ED), including convergent beam ED, has been used to determine atomic structure and charge distribution in crystals. Due to the strong dynamic effects of electron scattering, it is necessary to calculate ED with multiple scattering for quantitative analysis. So far, ED calculations are limited to crystals without modulation or with commensurate modulation (CM). For incommensurate modulation (IC), the ED is usually calculated using the approximant of a CM unit cell, which not only causes inaccuracy in results but also long computing time when the modulation wavevector **Q** is not along a major crystallographic axis. Here, we present direct ED calculations for crystals with IC based on Bloch wave method that has been widely used to calculate ED for simple crystals.

Modulated structures have periodic distortions of atomic position and/or occupation probability of atoms from their basic structure. These structures show additional sets of satellite reflections. The diffraction vector **H** of each spot can be written with reciprocal vectors **a***, **b***, **c*** in the reciprocal lattice of the basic structure and modulation wavevectors **Q** of the modulation wave as

$$\boldsymbol{H} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* + \sum_j^d m_j \boldsymbol{Q_j} = \boldsymbol{G} + \sum_j^d m_j \boldsymbol{Q_j} \quad (1)$$

Where **G** and $\mathbf{Q_j}$ (j=1, 2, …, d) are any basic reciprocal-lattice vector and the j[th] modulation wavevector, respectively; *h, k, l* and m_j are any integer. The structure factor of an IC structure can therefore be expressed in a simple form for displacive modulation [1]:

$$F(\boldsymbol{H}) = \sum_\mu f^\mu(\boldsymbol{H}) \exp\left(-\widetilde{\boldsymbol{H}} B_0^\mu \boldsymbol{H}\right) \exp\left(2\pi i \boldsymbol{G}\cdot \boldsymbol{r}_b^\mu\right) \int_0^1 dv \exp\{2\pi i[\boldsymbol{H}\cdot \boldsymbol{u}^\mu(v) + mv]\} \quad (2)$$

Where B_0^μ denotes Debye-Waller factor; $\boldsymbol{r}_b^\mu$ is the position of atom μ in the basic structure; $f^\mu(\boldsymbol{H})$ denotes the atomic scattering factor; $\boldsymbol{u}^\mu(v)$ is the atomic displacement; $v = \boldsymbol{Q}\cdot(\boldsymbol{T} + \boldsymbol{r}_b^\mu)$ with $\boldsymbol{T}$ the lattice vector. By using the structure factor calculated in eq. (2), we can solve the standard dispersion equation of high-energy electron diffraction in Bloch wave method, and then calculate the diffraction intensity [2]. A computer program based on above equations and Bloch wave method has been developed to calculate the ED for IC crystals (hereafter denoted as IC method).

We use High-T_c superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) to demonstrate the ED calculations for IC crystals. Bi2212 has an average structure with space group Bbmb and IC modulation $\boldsymbol{Q}$=0.21$\boldsymbol{b}^*$+$\boldsymbol{c}^*$ [3]. The modulation along the ***b*** direction is clearly seen in structure model and HRTEM image (Fig. 1). Image simulation (inset in Fig. 1b) with b_s=5b (b_s and b are lattice parameter along the b direction for supercell and average structure, respectively) supercell matches the experiment well. Fig. 2 compares the ED calculations based on CM approximation with that based on IC method. When the sample is thin, e.g. thickness=10 nm, the ED calculated by CM approximation (Fig. 2a) is very close to that by IC method (Fig. 2d). For thick sample, however, the difference between CM and IC becomes significant, as indicated by the red circles in Fig. 2b and 2e. Fig. 2g and 2h show the intensity profiles for main and satellite reflections as a function of the thickness. The difference between CM and IC is negligible when the sample is very thin (<5 nm), it becomes significant when the sample is thick where dynamical coupling among reflections becomes strong. It is therefore necessary to use IC method for quantitative ED analysis.

Moreover, because the large supercell in CM approximation, the calculations by CM approximation require much more computing resources, especially when the modulation wavevector is not along a major axis. For example, a second order modulation with $\mathbf{Q_1}$=0.27$\mathbf{b}^*$+0.945$\mathbf{c}^*$ and $\mathbf{Q_2}$=0.11$\mathbf{b}^*$-0.77$\mathbf{c}^*$ found in $LuFe_2O_{4+x}$ requires a minimum supercell with a_s=3.44 Å, b_s=64.73 Å and c_s=39.08 Å for CM approximation, which is basically impractical for Bloch wave calculations. With IC method we are able to calculate dynamical ED in minutes [4].

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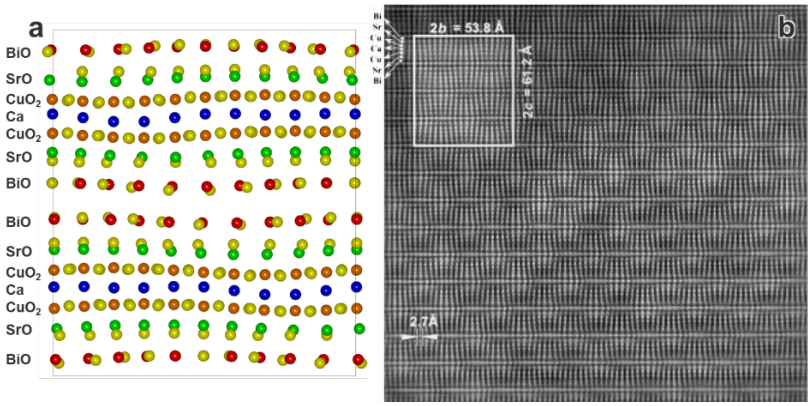

Figure 1. Structure model (a) and high resolution TEM image (b) of Bi2212 viewed along [100] direction, showing modulation along the ***b*** direction. The inset is the image simulation based on CM approximation.

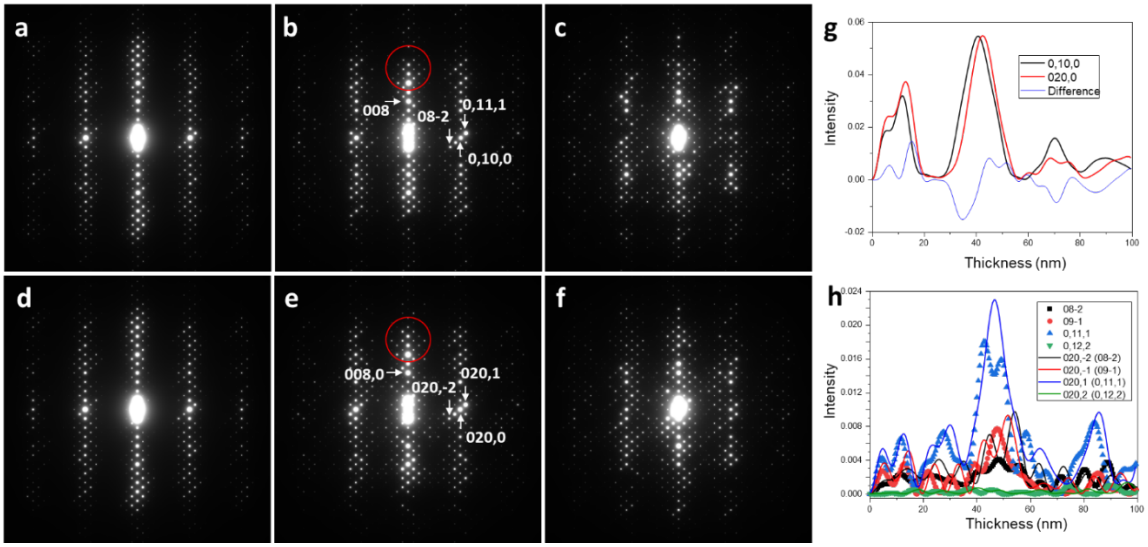

Figure 2. Electron diffraction patterns calculated along the [100] direction based on (a-c) 5b CM approximation of Bi2212 and (d-f) IC method at thickness of (a,d) 10 nm, (b,e) 50 nm and (c,f) 100 nm. (g,h) Intensity profile as a function of thickness for (g) main and (h) satellite reflections. The black and red lines in (g), and various symbols and solid lines in (h) are intensity profiles for CM approximation and IC, respectively. The blue line in (g) is the intensity difference between CM and IC.

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