

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

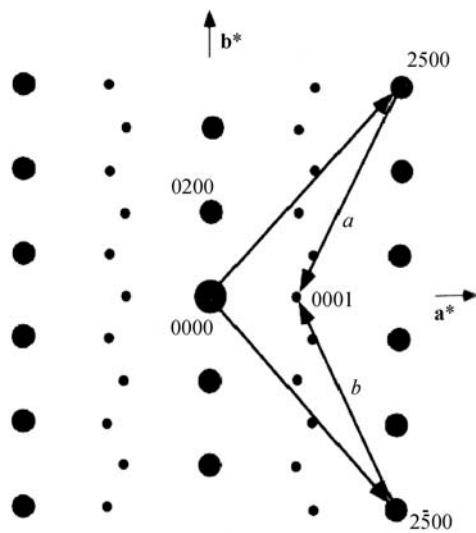


Fig. 2.5.3.22. Schematic diffraction pattern at the [001] incidence of $\text{Sr}_2\text{Nb}_2\text{O}_7$. *Umweganregung* paths *a* and *b* via fundamental reflections to the 0001 incommensurate reflection. Large and small spots denote fundamental and incommensurate reflections, respectively. The wave number vector of modulation is $\mathbf{k} = (\frac{1}{2} - \delta)\mathbf{a}^*$.

shown by crosses are kinematically forbidden by the glide plane ($\frac{c}{s}$) perpendicular to the *b* axis. *Umweganregung* paths *a*, *b* and *c* in the ZOLZ to a kinematically forbidden reflection are drawn. The two paths *a* and *b* are geometrically equivalent with respect to the line *m*-*m* perpendicular to the *b* axis. Since every *Umweganregung* path to a kinematically forbidden reflection contains an odd number of $F(0h_{2,i}h_{3,i}h_{4,i})$ with odd $h_{4,i}$, the following equation is obtained.

$$\begin{aligned} & F(0h_{2,1}h_{3,1}h_{4,1})F(0h_{2,2}h_{3,2}h_{4,2}) \dots F(0h_{2,n}h_{3,n}h_{4,n}) \quad \text{for path } a \\ & = -F(0\bar{h}_{2,1}h_{3,1}h_{4,1})F(0\bar{h}_{2,2}h_{3,2}h_{4,2}) \dots F(0\bar{h}_{2,n}h_{3,n}h_{4,n}) \\ & \text{for path } b, \end{aligned} \quad (2.5.3.12)$$

where $\sum_{i=1}^n h_{2,i} = 0$, $\sum_{i=1}^n h_{3,i} = h_3$ and $\sum_{i=1}^n h_{4,i} = h_4$ ($h_4 = \text{odd}$).

When reflection $00h_3h_4$ ($h_4 = \text{odd}$) is exactly excited, the two paths *a* and *c* are symmetric with respect to the bisector *m*'-*m*' of the diffraction vector of the reflection and have the same excitation error. The waves passing through these paths have the same amplitude but different signs. Thus the following relation is obtained.

$$\begin{aligned} & F(0h_{2,1}h_{3,1}h_{4,1})F(0h_{2,2}h_{3,2}h_{4,2}) \dots F(0h_{2,n}h_{3,n}h_{4,n}) \quad \text{for path } a \\ & = -F(0\bar{h}_{2,n}h_{3,n}h_{4,n})F(0\bar{h}_{2,n-1}h_{3,n-1}h_{4,n-1}) \dots F(0\bar{h}_{2,1}h_{3,1}h_{4,1}) \\ & \text{for path } c, \end{aligned} \quad (2.5.3.13)$$

where $\sum_{i=1}^n h_{2,i} = 0$, $\sum_{i=1}^n h_{3,i} = h_3$ and $\sum_{i=1}^n h_{4,i} = h_4$ ($h_4 = \text{odd}$).

Therefore, dynamical extinction occurs in kinematically forbidden reflections of incommensurate crystals. Fig. 2.5.3.21(b) schematically shows the extinction lines in odd-order incommensurate reflections, where the 0011 reflection is exactly excited.

We consider the dynamical extinction from $\text{Sr}_2\text{Nb}_2\text{O}_7$ whose space group is $P_{1s1}^{Cmc2_1}$. The glide plane ($\frac{c}{s}$) is perpendicular to the *b* axis with a glide vector $(\mathbf{c} + \mathbf{a}_4)/2$. The wave number vector of the modulation is $\mathbf{k} = (\frac{1}{2} - \delta)\mathbf{a}^*$. (Since space-group notation $Cmc2_1$ is broadly accepted, the direction of the modulation is taken as the *a* axis.) The reflections $h_10h_3h_4$ with $h_3 + h_4 = 2n + 1$ ($n = \text{integer}$) are kinematically forbidden. Fig. 2.5.3.22 shows a schematic diffraction pattern of $\text{Sr}_2\text{Nb}_2\text{O}_7$ at the [001] incidence. The large

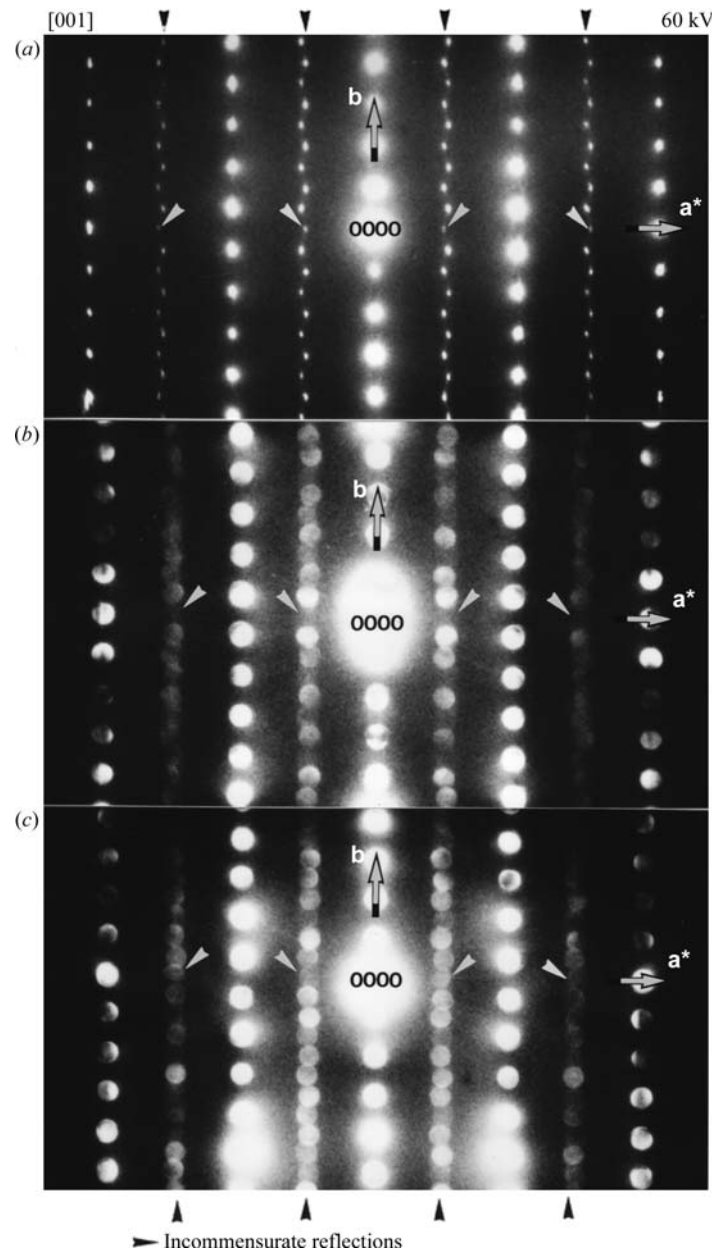


Fig. 2.5.3.23. Diffraction pattern of $\text{Sr}_2\text{Nb}_2\text{O}_7$ taken with [001] incidence at 60 kV. (a) Spot diffraction pattern. Kinematically forbidden 0001 and 2001 incommensurate reflections exhibit definite intensity. (b) Zone-axis CBED pattern showing dynamical absence of 0001 and 2001 incommensurate reflections. (c) CBED pattern taken at an incidence with a small tilt from the zone axis to the b^* direction. The kinematically forbidden incommensurate reflections have intensity due to incomplete cancellation of two waves through the *Umweganregung* paths. The wave number vector of modulation is $\mathbf{k} = (\frac{1}{2} - \delta)\mathbf{a}^*$.

and small spots indicate the fundamental ($h_4 = 0$) and incommensurate ($h_4 \neq 0$) reflections, respectively. *Umweganregung* paths *a* and *b* to the kinematically forbidden 0001 reflection via a fundamental reflection in the ZOLZ are drawn.

Fig. 2.5.3.23(a) shows a spot diffraction pattern of the incommensurate phase of $\text{Sr}_2\text{Nb}_2\text{O}_7$ taken with the [001] incidence at 60 kV. The incommensurate reflections in which dynamical extinction lines appear at this incidence are those with the indices $h_{1,\text{even}}00h_{4,\text{odd}}$ because $h_3 = 0$ and $h_1 + h_2 = 2n$ due to the lattice type *C* of the average structure.

The reflections in the four columns indicated by black arrowheads are incommensurate reflections. The reflections 0001, 000 $\bar{1}$, 200 $\bar{1}$ and $\bar{2}001$ designated by white arrowheads are kinematically forbidden but exhibit certain intensities, which are caused by multiple diffraction. Other reflections are fundamental reflections due to the average structure.