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TEM Image Contrast of 180° Domains of $BaTiO_3$

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Tanaka and Honjo [1] reported that ferroelectric 180° domains of $BaTiO_3$ do not show any contrast in the bright-field image but show conspicuous contrast in the 002 dark-field images as a result of the failure of Friedel's law, as is shown in Fig. 1. Similar contrast has been observed only in ferroelectric materials such as $PbTiO_3$, $KNbO_3$ and GeTe [2]. The contrast or the intensity difference between the adjacent 180° domains is formed by the difference of featureless background. Tanaka demonstrated in $PbTiO_3$ that the contrast increases as the specimen temperature approaches the Curie temperature [3], revealing the origin of the contrast to be thermal diffuse scattering (TDS). It should be noted that such contrast does not appear in strongly polar but non-ferroelectric materials, for example CdS [4]. This suggests that the specific thermal vibrations in ferroelectric materials give rise to the domain contrast. The contrast remains even if the images are taken by an ordinary electron microscope with the selector aperture put near the 002 Bragg spot. The zero energy-loss images of the domains taken by an energy-filtered TEM (JEM2010FEF) [5], in which plasmon-loss electrons are removed but TDS-loss electrons remain, show very slight contrast when the aperture is put at an off-Bragg position, but show distinct contrast when the aperture is put on the Bragg spot as shown in Fig. 2. This implies that the contrast is originated from the specific TDS very close to the Bragg spot ($\boldsymbol{q}$~0). It has been found that the contrast cannot be explained by the anomalous absorption effect in the dynamical theory of electron diffraction. Thus, the contrast can be interpleted as the failure of Friedel's law of the specific TDS, namely due to the third-order anharmonic effect of a soft-phonon mode (Slater mode).

Recently, Omoto et al. [6] developed a many-beam dynamical theory of inelastic scattering, which is applicable to non-centrosymmetric crystals. They calculated an asymmetric feature of Kikuchi patterns due to TDS generated from a polar crystal of CdS. We intend to explain the contrast of 180° domains of ferroelectric materials using Omoto's formula taking account of the anharmonic effect due to the Slater mode.

The intensity of inelastically scattered electrons is expressed as

$$\frac{dI_p^G}{d\Omega} = t\sum_{\lambda\lambda'}\sum_{\mu\mu'}\langle \boldsymbol{G}|p\lambda\rangle\langle p\lambda'|\boldsymbol{G}\rangle\,\langle 0\mu|\boldsymbol{O}\rangle\langle \boldsymbol{O}|0\mu'\rangle\,T_{\mu\mu'}^{\lambda\lambda'}\,\frac{\exp[\,it\gamma_{p\lambda\lambda'}\,]-\exp[\,it\gamma_{0\mu\mu'}\,]}{it(\gamma_{p\lambda\lambda'}-\gamma_{0\mu\mu'})},$$
$$T_{\mu\mu'}^{\lambda\lambda'} = \sum_{gh}\sum_{g'h'}\langle p\lambda|\boldsymbol{g}\rangle\langle \boldsymbol{g}'|p\lambda'\rangle\,T(\boldsymbol{Q},\boldsymbol{Q}')\,\langle \boldsymbol{h}|0\mu\rangle\langle 0\mu'|\boldsymbol{h}'\rangle, \tag{1}$$

where p is the scattered position in the 1st Brillouin zone, $\boldsymbol{G}$ is the reciprocal lattice vector, λ (μ) is index of Bloch wave and $\gamma_{p\lambda\lambda'} = \gamma_{p\lambda} - \gamma_{p\lambda'}$, $\gamma_{p\lambda}$ being the eigenvalue of λ'th Bloch wave at position p. $T(\boldsymbol{Q},\boldsymbol{Q}')$ is the mixed dynamic form factor (MDFF), expressed in eq. (4). TDS is expressed by the first order correlation of atomic vibrations for single phonon scattering (harmonic approximation) as

$$\left\langle e^{-iQu_\alpha+iQ'u_\beta}\right\rangle \approx 1+\frac{1}{2}\boldsymbol{Q}\left\langle \boldsymbol{u}_\alpha\boldsymbol{u}_\beta\right\rangle\boldsymbol{Q}'. \tag{2}$$

The second term of eq. (2) is written as

$$F_{\alpha\beta}(\boldsymbol{Q},\boldsymbol{Q}') = \sum_{q,j}\frac{\hbar\{n_{qj}+1/2\}}{2N\sqrt{m_\alpha m_\beta}\,\omega_{qj}}\,\boldsymbol{Q}\cdot\left(\boldsymbol{e}_{qj}^{\alpha\,*}\boldsymbol{e}_{qj}^{\beta}\right)\cdot\boldsymbol{Q}', \tag{3}$$

where $\boldsymbol{Q}$ and $\boldsymbol{Q}'$ are wave number vectors of inelastically scattered electrons, m_α is the mass of atom α, and j denotes the index of the branch of the phonon. The n_{qj} and $\boldsymbol{e}_{qj}$ are the number and polarization of the phonon with wave number vector $\boldsymbol{q}$ and frequency ω_{qj}. Using quantity (3), $T(\boldsymbol{Q},\boldsymbol{Q}')$ in eq. (1) is written as

$$T(\boldsymbol{Q},\boldsymbol{Q}') = \frac{1}{V_c}\sum_{\alpha}\sum_{\beta} f_\alpha(\boldsymbol{Q}) f_\beta(\boldsymbol{Q}') \exp[-i\boldsymbol{Q}\cdot\boldsymbol{r}_\alpha + i\boldsymbol{Q}'\cdot\boldsymbol{r}_\beta] \times 2F_{\alpha\beta}(\boldsymbol{Q},\boldsymbol{Q}') \exp[-W_\alpha(\boldsymbol{Q}) - W_\beta(\boldsymbol{Q}')], \tag{4}$$

where f, $\boldsymbol{r}$ and W are the atomic scattering factor for electrons, the position of the atom and the Debye-Waller factor, respectively. We consider the 3rd order cumulant term of eq. (2), that is,

$$\left\langle e^{-iQu_\alpha + iQ'u_\beta} \right\rangle \approx 1 + \frac{1}{2}\boldsymbol{Q}\left\langle \boldsymbol{u}_\alpha \boldsymbol{u}_\beta \right\rangle \boldsymbol{Q}' + \frac{i}{3!}\left\langle (-i\boldsymbol{Q}\cdot\boldsymbol{u}_\alpha + i\boldsymbol{Q}'\cdot\boldsymbol{u}_\beta)^3 \right\rangle . \tag{5}$$

The 3rd term of eq. (5) can give a positive (negative) contribution to TDS at $\boldsymbol{Q}$, but has a negative (positive) effect on TDS at $-\boldsymbol{Q}$. When we use the soft Slater mode, the TDS intensity can be enhanced by small ω_q through quantity (4). Using equation (5), quantity (3) is modified as follows:

$$\left\{1 + 2F_{\alpha\beta}(\boldsymbol{Q},\boldsymbol{Q}')\right\} \rightarrow \left\{1 + 2F_{\alpha\beta}(\boldsymbol{Q},\boldsymbol{Q}')\right\} \frac{i}{3!}\left\langle (-i\boldsymbol{Q}\cdot\boldsymbol{u}_\alpha + i\boldsymbol{Q}'\cdot\boldsymbol{u}_\beta)^3 \right\rangle . \tag{6}$$

Details will be reported at the meeting.

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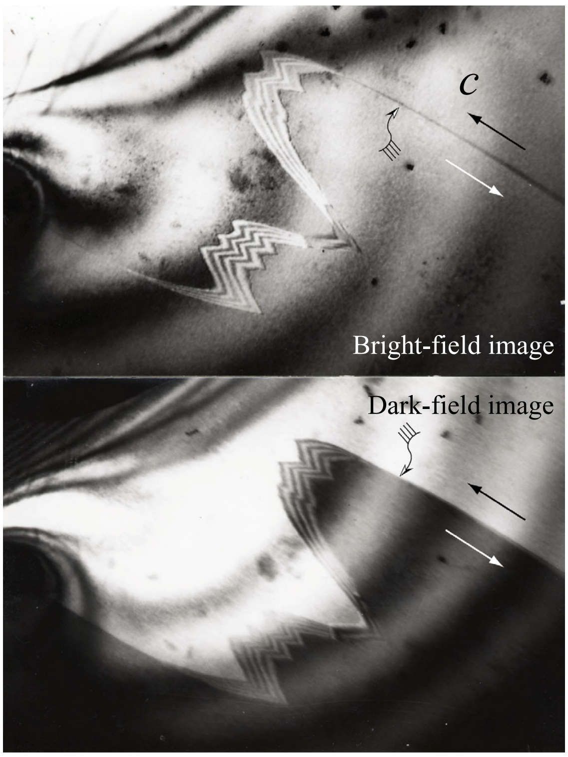


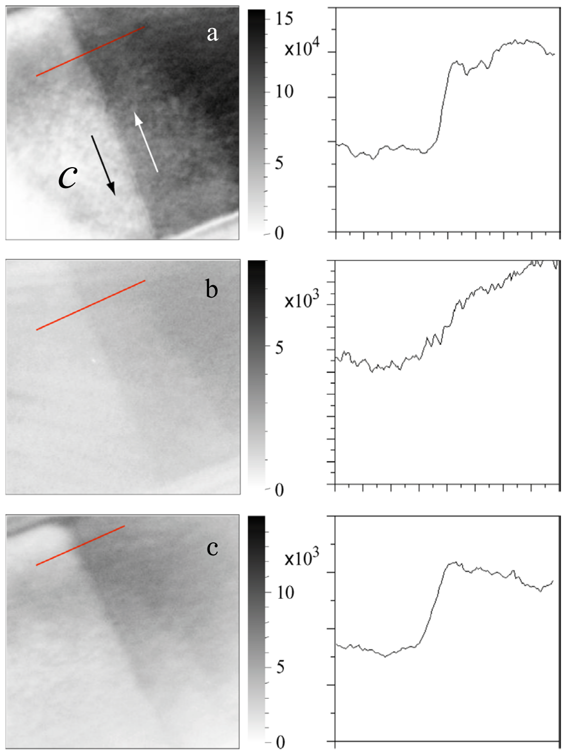
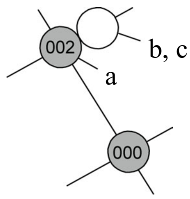


Figure 1(left): Ferroelectric 180° domains of $BaTiO_3$ (shown by arrows) contrast. No net contrast in the bright-field image but distinct one in the 002 dark-field image are noted.

Figure 2(right): 002 dark-field images of 180° domains of $BaTiO_3$. (a) Zero energy-loss image taken at the Bragg position, (b) TDS-loss image taken at an off-Bragg position and (c) plasmon-loss image taken at the off Bragg position. Distinct contrast is seen in (a) and (c).



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