

## TITLE → DIFFRACTION THEORY OF PHONON SCATTERED ELECTRONS

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Electron-phonon interactions are inelastic scattering processes in high-energy electron diffraction, and are responsible for thermal diffuse scattering (TDS). The atomic thermal vibrations introduce a small time-dependent perturbation to the crystal potential,

$$\Delta V(\mathbf{r}) = \sum_{\mathbf{h}} \sum_{\mathbf{l}} [v_{\mathbf{l}}(\mathbf{r}-\mathbf{R}(\mathbf{h})-\mathbf{r}(\mathbf{l})-\mathbf{u}(\mathbf{l}^{\mathbf{h}})) - v_{\mathbf{l}}(\mathbf{r}-\mathbf{R}(\mathbf{h})-\mathbf{r}(\mathbf{l}))], \quad (1)$$

where  $\mathbf{u}(\mathbf{l}^{\mathbf{h}})$  is the displacement of the  $\mathbf{l}^{\text{th}}$  atom (at position  $\mathbf{r}(\mathbf{l})$ ) within the  $\mathbf{h}^{\text{th}}$  unit cell (position  $\mathbf{R}(\mathbf{h})$ ) from its equilibrium position,

$$\mathbf{u}(\mathbf{l}^{\mathbf{h}}) = [(\hbar/2Nm_{\mathbf{l}})]^{1/2} \sum_{\mathbf{q}} \sum_{\mathbf{j}} [1/\omega_{\mathbf{j}}]^{1/2} \mathbf{e}(\mathbf{l} | \mathbf{q}) \exp\{i\mathbf{q} \cdot (\mathbf{R}(\mathbf{h}) + \mathbf{r}(\mathbf{l}))\} [a^{+}(\mathbf{q}_{\mathbf{j}}) + a(\mathbf{q}_{\mathbf{j}})]; \quad (2)$$

$v_{\mathbf{l}}$  is the potential of the  $\mathbf{l}^{\text{th}}$  atom;  $N$  is the total number of primitive unit cells in the crystal;  $m_{\mathbf{l}}$  is the mass of the  $\mathbf{l}^{\text{th}}$  atom;  $a^{+}$  and  $a$  are defined as the creation and annihilation operators of a phonon with wave vector  $\mathbf{q}$ , frequency  $\omega_{\mathbf{j}}(\mathbf{q})$  and polarization vector  $\mathbf{e}$ ; and  $\mathbf{j}$  indicates different phonon modes in the acoustic and optical branches. The interaction Hamiltonian for creating a phonon of momentum  $\mathbf{q}$  and frequency  $\omega_{\mathbf{j}}(\mathbf{q})$  is<sup>1</sup>

$$\begin{aligned} H'(\mathbf{r}, \mathbf{q}, \omega) &= \langle N(\mathbf{q}, \omega) + 1 | [-e \Delta V(\mathbf{r})] | N(\mathbf{q}, \omega) \rangle \\ &= -ie (2\pi)^3 \sum_{\mathbf{g}} A_{\mathbf{l}}(\omega_{\mathbf{j}}(\mathbf{q})) \mathbf{e}(\mathbf{l} | \mathbf{q}) \cdot (\mathbf{g}-\mathbf{q}) V_{\mathbf{l}}(\mathbf{g}-\mathbf{q}) \exp(i(\mathbf{q}-\mathbf{g}) \cdot \mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}(\mathbf{l})), \end{aligned} \quad (3)$$

where  $A_{\mathbf{l}}(\omega_{\mathbf{j}}(\mathbf{q})) \equiv [\hbar(N(\mathbf{q}, \omega) + 1)/2\omega_{\mathbf{j}}(\mathbf{q})m_{\mathbf{l}}N]^{1/2}$  and  $N(\mathbf{q}, \omega_{\mathbf{j}}) = 1/[\exp(\hbar\omega_{\mathbf{j}}/k_{\text{B}}T) - 1]$ . (4)

Since the life time of phonons ( $10^{-13}$  s) is much longer than the interaction time ( $10^{-16}$  to  $10^{-15}$  s for 100 keV) of fast electrons with a thin crystal, it is unnecessary to consider the time-dependent inelastic-state decay processes in electron scattering. Hence, the inelastic TDS wave  $\Psi_{\text{T}}$  generated by a single phonon ( $\mathbf{q}, \omega$ ) excitation is determined by<sup>2</sup>

$$(\nabla^2 - U_0(\mathbf{r}) + K^2)\Psi_{\text{T}} = (2\alpha_0/e)H'(\mathbf{r})\Psi_0, \quad (5)$$

where  $\Psi_0$  is the elastically scattered wave determined by the Schrödinger equation that can be solved using the multislice method, and  $\alpha_0 = me/\hbar^2$ . Under the small angle approximation, the solution of Eq. (5) at the exit face ( $z = d$ ) of a thin crystal is<sup>3</sup>

$$\Psi_{\text{T}}(\mathbf{b}, \mathbf{q}, d) \approx (\alpha_0 \Delta z / e) \sum_{\mathbf{n}} H'(\mathbf{b}, z_{\mathbf{n}}) Y(\mathbf{b}, \mathbf{q}, z_{\mathbf{n}}), \quad (6)$$

where  $Y(\mathbf{b}, \mathbf{q}, z) \equiv \Psi_0(\mathbf{r}, 0) \frac{\partial \Psi_0(\mathbf{r}, \mathbf{q})}{\partial z} \Psi_0(\mathbf{b}, z=d, \mathbf{q})$ ;  $\mathbf{b} = (x, y)$ ; and the summation of  $\mathbf{n}$  is over all the crystal slices of equal thickness  $\Delta z$ .

**The TDS diffraction pattern:** The TDS diffraction pattern is formed by the incoherent summation of all the TDS electrons after exciting different phonon modes ( $\mathbf{q}, \omega_{\mathbf{j}}$ ),

$$I_{\text{T}}(\tau) = [V_c / (2\pi)^3] \sum_{\mathbf{j}} \int_{\text{BZ}} d\mathbf{q} |\Psi_{\text{T}}(\tau, \mathbf{q}, d)|^2, \quad (7)$$

where  $V_c$  is the volume of the crystal;  $\tau = (\tau_x, \tau_y)$  is a 2-D reciprocal space vector; and the integration of  $\mathbf{q}$  is restricted to the first Brillouin zone (BZ). Neglecting the phase correlations of different Bragg spots  $\mathbf{g}$ s and the TDS waves generated at different depth  $z$ , one finally obtains,

$$I_{\text{T}}(\tau) = C_0 \sum_{\mathbf{n}} \sum_{\mathbf{j}} \{ B_{\mathbf{l}}(\mathbf{j}, \tau) | [e(\mathbf{l} | \mathbf{q}_{\mathbf{j}}) \cdot \tau] V_{\mathbf{l}}(\tau) |^2 \} \otimes \{ \sum_{\mathbf{g}} | Y(\tau, \mathbf{q}_0, z_{\mathbf{n}}) |^2 \}, \quad (8)$$

where  $B_{\mathbf{l}}(\mathbf{j}, \tau) \equiv \begin{cases} \int_{\text{BZ}} dq_z |A_{\mathbf{l}}(\omega_{\mathbf{j}}(\tau))|^2 & \text{if } \tau_x \text{ and } \tau_y \text{ fall within the first Brillouin zone (BZ);} \\ 0 & \text{otherwise;} \end{cases} \quad (9)$

$C_0 = (2\pi)^3 V_c (\alpha_0 \Delta z / S_c)^2$ ;  $S_c$  is the area of the unit cell cross-section in the  $x$ - $y$  plane;  $\mathbf{q}_0$  is the mean momentum transfer of the electrons in TDS; and  $\otimes$  indicates a 2-D convolution operation. In Eq. (8), the terms purely related to lattice dynamics are included in the first  $\{ \dots \}$  bracket. The terms purely related to the electron dynamical scattering appear in the second  $\{ \dots \}$  bracket. Therefore, dynamical diffraction effect does not affect the shapes of TDS streaks but does affect their intensities.

**A 2-D lattice vibration model:** For phonon excitations, since  $q_z = K\hbar\omega/2E \approx 0$ , the TDS streaks are mainly generated by the phonon modes with wave vectors parallel to the diffraction plane. These acoustic modes, for which  $\omega$  tends to zero when  $\mathbf{q}$  approaches zero, are mainly generated by the atomic vibrations within the plane perpendicular to the incident beam direction  $\mathbf{B} = [hkl]$  near a main crystal zone axis. This is actually a 2-D lattice vibration model. The main contributions to the TDS streaks are from the acoustic branches; optical branches contribute only a diffuse background. Thus the TDS streaks can be predicted by examining the terms in the first [...] bracket in Eq. (8), and is

$$S_{TDS} \equiv \sum_j B_j(j, \tau) - \sum_{j=1}^2 1/\omega_j(\tau), \quad (10)$$

where  $\omega_j(\tau)$  is the dispersion surface of the acoustic branches, and is determined by the 2-D atomic interactions of the nearest neighbors falling in the same (hkl) plane. The TDS streaks are defined by the  $\tau_x - \tau_y$  lines satisfying  $\omega_j(\tau) = 0$ . For a monatomic b.c.c. crystal oriented in [001], if only the interactions with the atoms located at  $\pm a_0(100)$  and  $\pm a_0(010)$  are considered, one has

$$(\omega_{1,2})^2 = (4/M) \{ (F+G) \sin^2(q_{x,y} a_0/2) + (F-G) \sin^2(q_{y,x} a_0/2) \}, \quad (11)$$

where  $a_0$  is the lattice constant, and  $F$  and  $G$  are the atomic force constants. In the central force approximation ( $F = G$ ), so that

$$S_{TDS} = \{ 1/\sin(\tau_x a_0/2) + 1/\sin(\tau_y a_0/2) \}. \quad (12)$$

Thus sharp TDS streaks should appear along  $\tau_x = 0$  ( $\{100\}$ ) and  $\tau_y = 0$  ( $\{010\}$ ) directions (see Fig. 1). The  $\langle 110 \rangle$  streaks would appear in the pattern if the phonon modes created by the vibrational coupling of the atoms located at (000) and  $a_0/2\{111\}$  were strongly excited. The absence of the  $\langle 110 \rangle$  streaks in Fig. 1 therefore supports the validity of the simplified 2-D model discussed above. In practice, the  $(F-G)$  term in Eq. (11) determines the streak sharpness and width. Therefore, the observed finite width of TDS streaks is mainly the result of non-central interaction forces. This 2-D model can systematically interpret the directions and sharpness of the TDS streaks observed in the diffraction patterns near the [001], [111] and [110] zone axes of Mo (b.c.c.), Au and Al (f.c.c.), and Si (diamond cubic). If  $\mathbf{B}$  is far from main zone axes, the contributions of optical branches may become important.

In practice, TDS streaks are located on the lines satisfying  $\tau \cdot \mathbf{r}_1 = 0$ , i.e., along the  $\tau = \mathbf{B} \times \mathbf{r}_1 = [(kL_1 - lK_1), (lH_1 - hL_1), (hK_1 - kH_1)]$  direction in reciprocal space, where  $\mathbf{r}_1 = (H_1 a_1, K_1 a_2, L_1 a_3)$  is the relative position of the first nearest neighbors in the 2-D plane, and  $a_i$  are crystal lattice constants.<sup>3</sup> This is a general rule for predicting TDS streaks without any numerical calculations, and is analogue to the  $\mathbf{g} \cdot \mathbf{b} = 0$  rule for determining dislocation Burgers vectors in diffraction contrast imaging. The TDS streaks predicted by this rule fit most the observations of Ni<sub>3</sub>Al, Al<sub>3</sub>Sc, NiAl and Fe<sub>3</sub>Al intermetallics.

**The TDS TEM image:** The HREM image formed by the TDS electrons in a TEM can also be derived from Eq. (6),

$$I_T(\mathbf{b}) = \left\{ \sum_n G^2(\mathbf{b}) |Y(\mathbf{b}, 0, z_n)|^2 \right\} \otimes |F_{OB}(\mathbf{b})|^2, \quad (13)$$

where the generation function of TDS is

$$G^2(\mathbf{b}, z_n) \equiv (\alpha_0 \Delta z)^2 \left\{ \sum_n \sum_l a_l^2 \left| \nabla_{v_l}(\mathbf{r} - \mathbf{R}(h) - \mathbf{r}(l)) \right|^2 \right\}; \quad (14)$$

where  $a_l^2 = \int d\omega \rho(\omega) A_l^2(\omega)$  is the atomic mean square vibration amplitude;  $\rho(\omega)$  is the phonon density of states; and  $F_{OB}$  is the inverse Fourier transform of the objective lens contrast transfer function. This formulation is equivalent to incoherent imaging theory. The image resolution may be higher than that formed purely by elastically scattered electrons, but the "inclined incidence effect" (i.e., a small off-axis correction of momentum transfer  $\mathbf{q}$  to incident wave vector  $\mathbf{K}$  in the elastic wave calculation) of phonon scattering may distort the image. The phase coupling of vibrating atoms does not affect the calculations for images but does affect diffraction patterns. Thus the image simulations can be carried out based on the Einstein model if the correct vibration amplitude for each atom is used.

It can be proved from Eqs. (3) and (6) that the semi-classical approach utilizing a "frozen" lattice model for TDS is equivalent to the result of inelastic quantum scattering theory (Eq. (8)) if  $k_B T \ll \hbar\omega$  and the "inclined incidence effect" is negligible. The former condition is satisfied if the temperature is not much higher than room temperature.<sup>4</sup>

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4. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

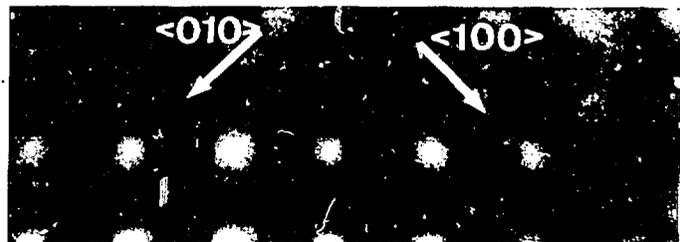


FIG. 1.--Diffraction pattern of Mo [001].