Determination of phonon dispersion relations by X-ray thermal diffuse scattering

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Abstract. Thermal diffuse scattering (TDS) of X-rays from crystals contains information on phonons. This paper reviews the general theory of TDS and some recent experiments aimed at further developing TDS into a useful and efficient method for studying phonon dispersion relations.

Introduction

X-ray thermal diffuse scattering (TDS) refers to scattering caused by lattice thermal vibrations, i.e., phonons. Unlike Bragg diffraction which is characterized by sharp peaks in k space, TDS is diffusely distributed due to the continuous distribution of phonon modes. For crystallographers interested in Bragg diffraction, TDS is often considered a nuisance, or a background that must be removed from the data. Yet TDS can be valuable for determining phonon dispersion relations.

The effect of thermal vibration on X-ray scattering was first investigated by Debye [1] who introduced a temperature factor exp (−2M) to the intensity of X-ray reflections. The idea was later developed in more detail by Faxén [2] and Waller [3]. But it was not until the work of Laval [4] and Zachariasen [5] in about 1940 that the relationship between TDS intensity and lattice vibration was firmly established. The theory was further developed by Born [6] and the subject was comprehensively reviewed by James [7] in 1945. The first experiment to determine phonon dispersion relations from TDS was performed by Olmer on aluminum [8] in 1948. Similar measurements were carried out in the 1950s for other simple metals including α-iron [9], zinc [10], copper [11], and aluminum again [12]. Also investigated were some compounds including, e.g., β-brass [13], AgCl [14], KCl [15] and NaCl [16]. A historical survey of the early developments can be found in Wooster's book [17]. Other reviews on TDS include, but are not limited to, the publications of Zachariasen [18], Slater [19], Cochran [20], Maradudin et al. [21], Warren [22], Krivoglaz [23], and Willis and Pryor [24].

The cross section for TDS is small. Early TDS experiments were performed with X-ray tubes, yielding a rather slow data acquisition rate of about one hour per point in reciprocal space [12]. Therefore, early measurements were typically limited to high-symmetry directions. Quantitative analysis was difficult and usually involved force constants up to the second or third nearest-neighbors only, even though more distant neighbors were clearly needed in most cases. The accuracy of the results was thus limited. These limitations made this method relatively impractical. With the advent of the neutron scattering technique in the 1950s, the TDS method was largely abandoned. Nevertheless, a few studies were carried out in the ensuing years on V [25], InAs [26], and VSi [27].

Recent years have seen the situation turned around. Third generation synchrotron radiation sources provide highly collimated beams with an intensity many orders of magnitude higher than that of X-ray tubes. Two-dimensional X-ray detectors such as image plates and CCD cameras allow parallel measurements over a large solid angle. It is now feasible to carry out TDS measurements with high precision and efficiency. Furthermore, modern computational capabilities enable efficient quantitative analysis of experimental data with sophisticated modeling. Recent experiments on Si [28, 29], TiSe2 [30] and Nb [31] have confirmed TDS as a practical technique for phonon dispersion measurements.

At present, there are three complementary methods for phonon studies: TDS, neutron scattering, and inelastic X-ray scattering (which is another method made practical by the improvement in X-ray source intensity). Compared with the other two techniques, TDS has the advantages of a high data-acquisition rate and a simple experimental setup. The X-ray methods are also much better suited for small crystals, materials that are only available in polycrystalline forms, and samples contained in high-pressure cells, as it is fairly easy to focus X-rays to a small spot size. Neutron scattering, by contrast, typically requires sample sizes in the ~1 cm range. Certain materials such as Pu have a high neutron absorption cross section, and
X-ray methods are the only practical choices. The energy and polarization of X-rays can be easily tuned, which can be very useful for certain types of measurements.

In the following section we review the theory of TDS. Explicit formulae are presented. This is followed by a review of recent experimental work to illustrate the progress made. The paper concludes with a summary and a few comments about possible future developments.

**Theory**

Formulae for X-ray TDS intensities from monatomic crystals, i.e., crystals with one atom per unit cell, are available from several references (e.g., Refs. [7, 21, 22]). The case is more complicated for crystals with a multi-atom basis, because the results depend on the definition of the dynamic matrix. Most articles on this subject are incomplete, often with this important definition missing. A fairly detailed derivation is available in Ref. [24], but there are several errors. The following discussion includes the key formulae needed for developing numerical algorithms for analyzing TDS results.

Consider a crystal with $N$ unit cells, each with $n$ atoms. Let $\mathbf{r}_{m,s} = \mathbf{R}_m + \mathbf{t}_s + \mathbf{u}_{m,s}$ be the position vector of the $s$-th atom in the $m$-th unit cell, where $\mathbf{R}_m$ is the lattice vector, $\mathbf{t}_s$ is the atomic basis vector within a unit cell, and $\mathbf{u}_{m,s}$ is the displacement of the atom from its equilibrium position due to thermal vibration. In the harmonic approximation, the crystal potential energy becomes

$$U = U_0 + \frac{1}{2} \sum_{m,m',s,s'} n \sum_{s,s'} \left( \frac{\partial^2 U}{\partial \mathbf{r}_{m,s} \partial \mathbf{r}_{m',s'}} \cdot \mathbf{u}_{m,s} \cdot \mathbf{u}_{m',s'} \right).$$

The Born-von Karman force constants are defined as

$$\Phi^{\alpha,\beta}_{m,s,m',s'} = -\frac{\partial^2 U}{\partial \mathbf{r}_{m,s} \partial \mathbf{r}_{m',s'}},$$

where indices $\alpha, \beta = x, y$ or $z$. Because of the translational symmetry of the crystal, $\Phi^{\alpha,\beta}_{m,s,m',s'}$ functions of $\mathbf{R}_{m'} - \mathbf{R}_m$ (abbreviate as $\mathbf{R}_{m,m'}$).

Let $\mu_i$ be the mass of the $s$-th atom. The equation of motion for each atom is given by

$$\mu_i \ddot{\mathbf{u}}_{i,m,s} = \sum_{m',s'} \Phi^{\alpha,\beta}_{m,s,m',s'} \cdot \mathbf{u}_{m',s'}.$$

Solutions are sought with the form

$$\mathbf{u}_{m,s} = \text{Re} \left\{ \frac{1}{\sqrt{\mu_s}} a_k \mathbf{e}_{k,s} e^{i \omega_k t} \right\},$$

where $\mathbf{k}, \omega_k, a_k$ and $\mathbf{e}_{k,s}$ are the wave vector (in the first Brillouin zone), frequency, vibration amplitude, and polarization vector associated with the $s$-th atom, respectively. This turns Eq. (3) into an eigenvalue equation

$$\mathbf{D}(\mathbf{k}) \cdot \mathbf{e}_{k,j} = \omega_k^2 \mathbf{e}_{k,j},$$

where $j = 1, 2, \ldots, 3n$ labels different phonon branches with the same wave vector $\mathbf{k}$. The dynamical matrix ($\mathbf{D}$ matrix) $\mathbf{D}(\mathbf{k})$ is a $3n \times 3n$ matrix whose elements are given by

$$D_{\alpha,\beta}^{\gamma,\delta}(\mathbf{k}) = -\sum_{m'} \frac{\phi^{\alpha,\beta}_{m,s,m',s'}}{\sqrt{\mu_s \mu_{s'}}} \exp \left[ i \mathbf{k} \cdot (\mathbf{R}_{m,m'} + \mathbf{t}_s + \mathbf{t}_{s'}) \right],$$

where $\mathbf{t}_s + \mathbf{t}_{s'}$ stands for $\mathbf{t}_s - \mathbf{t}_{s'}$. Because of translational symmetry, one could set $\mathbf{R}_m = 0$ in the above equation for simplicity. The eigenvectors $\mathbf{e}_{k,j}$ are defined as

$$\mathbf{e}_{k,j} = \left( \mathbf{e}_{k,j,1}, \mathbf{e}_{k,j,2}, \ldots \right),$$

which satisfy the orthonormal relationship

$$\mathbf{e}_{k,j} \cdot \mathbf{e}_{k,j'}^* = \sum_s \mathbf{e}_{k,j,s}^* \cdot \mathbf{e}_{k,j',s} = \delta_{j,j'}.$$

With these definitions, $\mathbf{D}(\mathbf{k})$ and $\mathbf{e}_{k,j}$ are not periodic in reciprocal space. Denoting a reciprocal lattice vector by $\mathbf{K}$, we have

$$\mathbf{D}_{s,s'}(\mathbf{k} + \mathbf{K}) = \mathbf{D}_{s,s'}(\mathbf{k}) \exp \left( i \mathbf{K} \cdot \mathbf{t}_s \right),$$

$$\mathbf{e}_{k + \mathbf{K},j} = \mathbf{e}_{k,j} \exp \left( -i \mathbf{K} \cdot \mathbf{t}_s \right).$$

The dynamical matrix can be defined in a different manner, yielding a periodic quantity. Consider the following alternative definition for the lattice wave in Eq. (4):

$$\mathbf{u}_{m,s}^C = \text{Re} \left\{ \frac{1}{\sqrt{\mu_s}} a_k \mathbf{e}_{k,s} e^{i \omega_k t} \right\}.$$

Here, the atomic basis vectors are not included in the lattice Fourier transformation. The resulting dynamic matrix, known as the C matrix, is given by

$$C_{s,s'}^{\alpha,\beta}(\mathbf{k}) = -\frac{1}{\sqrt{\mu_s \mu_{s'}}} \sum_{m'} \phi^{\alpha,\beta}_{m,s,m',s'} \exp \left( i \mathbf{k} \cdot \mathbf{R}_{m,m'} \right).$$

As before, one could set $\mathbf{R}_{m} = 0$ for simplicity. The eigenvalue equation is the same as Eq. (5), but the resulting eigenvectors $\mathbf{e}_{k,j}^C$ differ from the ones based on the D matrix by a phase factor:

$$\mathbf{e}_{k,j}^C = \mathbf{e}_{k,j} \exp \left( i \mathbf{K} \cdot \mathbf{t}_s \right).$$

We will primarily use the D matrix in our discussion. Some final results will also be presented in terms of the C matrix.

Let $f_s$ be the atomic scattering factor of the $s$-th atom in a unit cell and $\mathbf{q}$ be the X-ray scattering vector, i.e., difference between the outgoing and incident wave vectors. The time-averaged intensity of the scattered wave by the crystal is given by

$$I(q) = I_0 \left\{ \left| \sum_{m,s} f_s \exp \left[ i \mathbf{q} \cdot (\mathbf{R}_m + \mathbf{t}_s + \mathbf{u}_{m,s}) \right] \right|^2 \right\},$$

$$= I_0 \sum_{m,m',s,s'} \left| f_{s,s'} \exp \left[ -i \mathbf{q} \cdot (\mathbf{R}_{m,m'} + \mathbf{t}_s + \mathbf{t}_{s'}) \right] \right|^2,$$

$$\times \exp \left[ -\frac{1}{2} \left( \mathbf{q} \cdot (\mathbf{u}_{m,s} - \mathbf{u}_{m',s'}) \right)^2 \right].$$
Profoundly inspired, this approach demonstrates, *i.e.*, Warren’s book [22]. In the above equation, $I_0$ is the intensity of scattering from a single electron. For a linearly-polarized incident beam [22],

$$I_0 = \frac{e^4}{m_e^2 c^2 d^2} \left[ \sin^2 \phi + \cos^2 \phi \cos^2 (2\theta) \right],$$

(15)

where $I_{inc}$ is the incident beam intensity, $m_e$ is the electron mass, $d$ is the distance from the scattering center to the detector, $2\theta$ is the scattering angle, and $\phi$ is the azimuthal angle between the polarization of the incident beam and the scattering plane. For an unpolarized incident beam,

$$I_0 = \frac{e^4}{m_e^2 c^2 d^2} \left[ 1 + \cos^2 (2\theta) \right].$$

(16)

The atomic displacement $u_{m,s}$ is a superposition of all lattice vibration modes:

$$u_{m,s} = \text{Re} \left\{ \frac{1}{\sqrt{\mu_s}} \sum_{k,j} \{ a_{k,j} c_{k,j} \} \exp \left[ i \mathbf{k} \cdot (\mathbf{R}_m + \mathbf{t}_s) - i \omega_{k,j} \mathbf{t} + i \phi_{k,j} \mathbf{t} \right] \right\}. \quad (17)$$

The phases $\phi_{k,j}$ are independent random variables for different modes. The cross terms involving different modes thus time average to zero. With this simplification,

$$\frac{1}{2} \langle \mathbf{q} \cdot (u_{m,s} - u_{m',s'}) \rangle^2 = M_s + M_s' - \sum_{k,j} \frac{|a_{k,j}|^2}{\sqrt{\mu_s \mu_{s'}}} \left\{ \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle^2 - \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle' \right\} \exp \left[ i \mathbf{k} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right]. \quad (18)$$

where the Debye-Waller factor $M_s$ is defined as

$$M_s = \frac{1}{4 \mu_s} \sum_{k,j} |a_{k,j}|^2 |\mathbf{q} \cdot \mathbf{c}_{k,j}|^2. \quad (19)$$

For a cubic system, $M_s$ depends on the magnitude of $\mathbf{q}$ only [32], and the above equation becomes

$$M_s = \frac{q^2}{12 \mu_s} \sum_{k,j} |a_{k,j}|^2 |\mathbf{q} \cdot \mathbf{c}_{k,j}|^2. \quad (20)$$

The square amplitudes $|a_{k,j}|^2$ is evaluated by considering the mean kinetic energy of the system

$$\langle KE \rangle = \frac{1}{2} \sum_{m,s} \mu_s (\mathbf{u}_m^2) = \frac{N}{4} \sum_{k,j} |a_{k,j}|^2 \omega_{k,j}^2. \quad (21)$$

Based on the quantum theory of harmonic oscillators, the mean total energy is

$$\langle E \rangle = 2 \langle KE \rangle = \sum_{k,j} \frac{\hbar \omega_{k,j}}{\sqrt{\hbar^2 \omega_{k,j}^2 + 1} \hbar^2 \omega_{k,j}^2}. \quad (22)$$

Comparing Eqs. (21) and (22), we obtain

$$|a_{k,j}|^2 = \frac{\hbar}{N \omega_{k,j}} \coth \left( \frac{\hbar \omega_{k,j}}{2k_B T} \right). \quad (23)$$

Equation (14) becomes

$$I(\mathbf{q}) = N I_0 \sum_{m,s} \sum_{x',y'} \left\{ f_{x'z} \exp \left( -M_s - M_{s'} \right) \times \exp \left[ -i \mathbf{q} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right] \exp \left[ G_{m.s',x'}(\mathbf{q}) \right] \right\}, \quad (24)$$

where

$$G_{m.s',x'}(\mathbf{q}) = \frac{\hbar}{2N \sqrt{\mu_s \mu_{s'}}} \sum_{k,j} \left\{ \frac{1}{\omega_{k,j}} \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle^2 \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle' \right\} \times \coth \left( \frac{\hbar \omega_{k,j}}{2k_B T} \right) \exp \left[ i \mathbf{k} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right]. \quad (25)$$

In deriving Eq. (15), we’ve set $\mathbf{R}_m = 0$ in view of the translational symmetry, and have simplified the notation by substituting $\mathbf{R}_m$ for $\mathbf{R}_m'$. This is the general formula of X-ray TDS intensity from a single crystal within the harmonic approximation. The expression for $G$ is different if the derivation is made with the C matrix:

$$G^C_{m,s',x'}(\mathbf{q}) = \frac{\hbar}{2N \sqrt{\mu_s \mu_{s'}}} \sum_{k,j} \left\{ \frac{1}{\omega_{k,j}} \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle^2 \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle' \right\} \times \coth \left( \frac{\hbar \omega_{k,j}}{2k_B T} \right) \exp \left[ i \mathbf{k} \cdot \mathbf{R}_m \right]. \quad (26)$$

The above intensity formulae, while simple and elegant, are not necessarily practical for numerical purposes. It requires three-dimensional sums in both reciprocal and real spaces for each $\mathbf{q}$ vector. It is generally too computationally demanding even with a fairly powerful modern computer. Further simplification can be achieved by treating $G$ as a small quantity and using the relation

$$\exp \left( x \right) = 1 + x + x^2 / 2 + \ldots,$$

to expand $I(\mathbf{q})$ as a series of terms:

$$I(\mathbf{q}) = I_0 + I_1 + I_2 + \ldots. \quad (27)$$

$$I_0 = N I_0 \sum_{m,s,x'} \left\{ f_{x'z} \exp \left( -M_s - M_{s'} \right) \right\} \times \exp \left[ -i \mathbf{q} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right], \quad (28)$$

$$I_1 = N I_0 \sum_{m,s,x'} \left\{ f_{x'z} \exp \left( -M_s - M_{s'} \right) \right\} \times \exp \left[ -i \mathbf{q} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right] G_{m.s',x'}(\mathbf{q}), \quad (29)$$

$$I_2 = N I_0 \sum_{x',y'} \left\{ f_{x'z} \exp \left( -M_s - M_{s'} \right) \right\} \times \exp \left[ -i \mathbf{q} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right] G_{m,s',x'}(\mathbf{q}). \quad (30)$$

The 0-th order term $I_0$ corresponds to Bragg diffraction. The other terms correspond to first-order TDS, second-order TDS, etc. These TDS terms are generally nonzero for any $\mathbf{q}$.

The first-order term is often the dominant contribution to TDS, especially at modest or low temperatures. An important property of the scattering intensity $I(\mathbf{q})$ is that it depends only on phonons with the same wave vector $\mathbf{q}$. The full expression of $I_1$ is given by

$$I_1 = \frac{\hbar I_0}{2 \sqrt{\mu_s \mu_{s'}}} \sum_{m,s,x'} \left\{ \frac{f_{x'z}}{\sqrt{\hbar^2 \omega_{k,j}^2 + 1} \hbar^2 \omega_{k,j}^2} \right\} \times \left\{ \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle^2 \langle \mathbf{q} \cdot \mathbf{c}_{k,j} \rangle' \right\} \coth \left( \frac{\hbar \omega_{k,j}}{2k_B T} \right) \exp \left[ i \mathbf{k} \cdot (\mathbf{R}_m + \mathbf{t}_s) \right]. \quad (31)$$
Using the identity
\[ \sum_{m=1}^{N} e^{i \mathbf{k} \cdot \mathbf{R}_m} = N \sum_{l=1}^{N} \delta_{\mathbf{k}, \mathbf{k}_l}, \]
with \( \mathbf{k} \) denoting the reciprocal lattice vectors, the above equation can be reduced to
\[
I_1 = \frac{\hbar N \ell_e}{2} \sum_i \frac{1}{\omega_{q,i}} \coth \left( \frac{\hbar \omega_{q,i}}{2k_B T} \right) \sum_{k=q-K_q}\left| F_j(q) \right|^2.
\]
where \( K_q \) denotes the nearest reciprocal lattice vector to \( q \), and \( \mathbf{k} = q - K_q \) is the reduced wave vector of \( q \) in the first Brillouin zone. Making use of Eq. (10), we define the one-phonon structure factor as
\[
F_j(q) = \sum_i \frac{f_j}{\sqrt{\mu_s}} \exp (-M_j) (q \cdot \mathbf{e}_{q,j,i}) \exp (-i \mathbf{K}_q \cdot \mathbf{r}_i).
\]
All quantities are evaluated at \( q \) in Eq. (33). The first-order TDS intensity becomes
\[
I_1(q) = \frac{\hbar N \ell_e}{2} \sum_i \frac{1}{\omega_{q,i}} \coth \left( \frac{\hbar \omega_{q,i}}{2k_B T} \right) \left| F_j(q) \right|^2.
\]
The intensity formula remains unchanged if derived with the \( C \) matrix, but the structure factor becomes
\[
F^C_j(q) = \sum_i \frac{f_j}{\sqrt{\mu_s}} \exp (-M_j) (q \cdot \mathbf{e}_{q,j,i}) \exp (-i \mathbf{K}_q \cdot \mathbf{r}_i).
\]
Equation (34) contains no three-dimensional sums and is therefore easy to evaluate numerically.

A formula for second-order TDS can be similarly derived to yield
\[
I_2(q) = \frac{\hbar^2 L V}{8} \int \frac{d^3 k}{(2\pi)^3} \sum_{j,j'} \Omega_{k,j} \Omega_{q-k,j'} \left| P_{j,j'}(q,k) \right|^2,
\]
where
\[
\Omega_{k,j} = \frac{1}{\omega_{k,j}} \coth \left( \frac{\hbar \omega_{k,j}}{2k_B T} \right),
\]
\[
P_{j,j'}(q,k) = \sum_s \frac{f_s}{\mu_s} \exp (-M_s) (q \cdot \mathbf{e}_{k,j,s}) (q \cdot \mathbf{e}_{q-k,j',s}).
\]
\[
V \text{ is the volume of the crystal (illuminated by the incident beam), and the integration is over the first Brillouin zone. If the C matrix is used instead, the last equation is replaced by}
\[
P^C_{j,j'}(q,k) = \sum_s \frac{f_s}{\mu_s} \exp (-M_s) (q \cdot \mathbf{e}^C_{k,j,s}) (q \cdot \mathbf{e}^C_{q-k,j',s}) \exp (-i q \cdot \mathbf{r}_j).
\]
Evaluation of second-order TDS involves a Brillouin-zone sum or integral, and is therefore much more computationally demanding than the first-order case. Approximations can be made to simplify the computation at the expense of accuracy [22].

**Recent experiments**

Having been largely ignored for decades, the TDS method was reexamined in 1999 by Wu et al. [33], who reported a study of TDS patterns obtained from a single crystal Si using intense X-rays derived from a third-generation light source. The main features in the TDS pattern were well explained by the phonon dispersion relations of Si. Similar patterns were also observed by Hastings at about the same time [34].

The reverse process, i.e., determining phonon dispersion relations from TDS patterns, was carried out by Holt et al. [28, 29]. The experiment was done in the same manner as the previous work, with a Si crystal at room temperature scattering a monochromatic synchrotron X-ray beam in a transmission Laue geometry. Two dimensional TDS patterns were recorded with an image plate, as shown in Figs. 1a and 1b, for Si(111) and Si(100). Each pixel in these images corresponds to a scattering vector \( q \) on the Ewald sphere cutting through the reciprocal space. The dark shadows in the images came from a circular beam stop and its post. The bright spot at the center of each beam stop shadow is caused by the remnant of the direct beam. The spot size is an indication of the beam diameter. Clear threefold and fourfold symmetries of the TDS patterns can be seen in Figs. 1a and 1b, respectively, as expected. The energy of the X-ray beam was selected so that no Bragg conditions were satisfied throughout the area of detection. The bright spots in the TDS images correspond to points on the Ewald sphere close to reciprocal lattice points, where the acoustic phonon populations are high. For first order scattering, the TDS intensity from each phonon mode is directly proportional to the thermal population of phonons (including the zero-point vibration effect). A low frequency mode, such as an acoustic mode near a reciprocal lattice point, has a high thermal population and thus yields a high TDS intensity.

An analysis leading to phonon dispersion curves was carried out by Holt et al. in the following manner. A Born-von Karman model with force constants up to the sixth neighbor was employed to calculate the phonon eigenvalues and eigenvectors. Equation (34) was then employed to calculate theoretical TDS patterns, which were then fitted to the experimental images by a least-squares procedure with the force constants as fitting parameters. Figs. 1c and 1d are the results of the fit. No discernable differences exist between the theoretical and experimental images. The fitting procedure is essentially equivalent to numerically solving Eq. (34) to yield the phonon frequencies as a function of momentum transfer.

Attenuation of the incident and scattered beams by the sample and background scattering intensity must be accounted for in calculating theoretical TDS intensities, as indicated by the following equation:
\[
I_{\text{theory}} = \cos (2\theta) T(\theta, \phi) [A I_1 + B I_e + C(\theta)] + D, \tag{40}
\]
where \( I_1 \) is the first-order intensity calculated from Eq. (34).
In the above equation, $T(\theta, \phi)$ accounts for sample attenuation based on the total path length, and is easily computed. $A$ is an intensity normalization factor. The terms containing $B$ and $C$ together represent a background from higher order, defect, and Compton scattering of the sample. For the analysis of the Si results, $B$ was taken to be a constant, and $C$ was taken to be zero. $D$ is an overall constant background due to detector noise. The cos $(2\theta)$ factor in front of the formula stands for solid angle conversion associated with planar projection on a flat detector. Equation (16) contains additional angular factors that must be included in a full analysis. For the Si work, quantities that were unknown or could not be precisely measured were set as fitting parameters, including the three Euler angles for the crystal orientation, the exact distance from the sample to the detector plane, and parameters for intensity normalization and the background functions.

The fit to the Si TDS images yields phonon dispersion relations in excellent agreement with available neutron scattering results, as seen in Fig. 2. The two images in Fig. 1 were obtained with an exposure time of 10 s each. Thus, the data collection efficiency of the method is very high.

A consequence of the thermal population factor $\coth(\hbar\omega/2kBT)$ in Eq. (34) is that phonon modes with lower frequencies give rise to higher scattering intensities. This effect is amplified by the $1/\omega$ dependence of the cross section as indicated by the same equation. A simple procedure to partially compensate for this bias in the least-squares fitting is to work with a logarithmic scale for the scattering intensity. The rich structures in Fig. 1 are a result of the use of a logarithmic scale, which gives the TDS images enhanced sensitivity to phonons at higher frequencies. As an illustration, Figs. 1e and 1f show the same theoretical

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**Fig. 1.** Experimental TDS images for (a) Si(111) and (b) Si(100) as well as theoretical first-order TDS images for (c) Si(111) and (d) Si(100). The theoretical images are calculated with a sixth-nearest-neighbor Born-von Karman force constant model. (e) and (f) show theoretical images with the three optical phonon branches ignored.

**Fig. 2.** Phonon dispersion curves of Si. Circles are neutron scattering data. Solid curves are results derived from best fits to the TDS patterns.
images of Si(111) and Si(100) as Figs. 1c and 1d, but with all three optical phonon branches excluded from the calculation. Differences between corresponding pairs of theoretical images are apparent. If the images were displayed using a linear scale, the differences would be essentially indiscernible.

The same technique was later applied to Nb [31] as another test for the method. Nb is an interesting case, since its phonon dispersion relations have a number of pronounced anomalies caused by strong electron-phonon interactions. Results of a fit of a theoretical model to the TDS patterns are shown in Fig. 3. Although not quite as impressive as the Si case, there is still a fairly good agreement between the fit and the neutron scattering data, especially at low frequencies. The discrepancies could be due to limitations of the force constant model used or due to the lesser quality of the crystal compared to Si. Further research is needed to understand the reasons for the discrepancies.

In another experiment Holt et al. applied TDS to study the phonon softening phenomenon in TiSe$_2$ [30]. This material has a charge-density wave transition at $\sim$$200$ K, which results in a commensurate $(2 \times 2 \times 2)$ superlattice at lower temperatures. The transition involves a softening of the $L_A$ phonon mode at the zone boundary. This softening behavior, however, had not been examined in detail by experiment. Neutron scattering was attempted, but a poor signal-to-noise ratio and an intense central peak made it difficult to perform a quantitative analysis. Instead of taking two-dimensional images, Holt et al. took linear scans in $k$ space along the $A$–$L$–$A$ direction. As the sample temperature was lowered from room temperature to the transition temperature $T_c$, the TDS intensities near the $L$ point increased due to the softening of the phonon mode. A Bragg peak emerged at $T_c$ and became more intense as the temperature was further reduced. Quantitative analysis was performed by fitting a force constant model to the TDS data. The resulting dispersion curves in the $A$–$L$ direction for various temperatures are presented in Fig. 4. The lowest phonon branch softens with a power law in agreement with the prediction of a mean field theory, which is expected for this system.

**Fig. 3.** Phonon dispersion curves of Nb. Open circles are neutron scattering data. Solid curves are derived from a best fit to the TDS patterns based on an eighth-nearest-neighbor Born-von Karman model.

**Fig. 4.** Phonon dispersions curves of TiSe$_2$ as a function of temperature deduced from X-ray TDS.

**Comments and concluding remarks**

Unlike neutron scattering or inelastic X-ray scattering methods which make direct measurements of phonon dispersion relations, TDS, as discussed above, is an indirect method. It relies on fitting the data using calculated intensities based on a model, such as the Born-von Karman force constant model. The numerical analysis and fitting can be time consuming. A TDS image typically consists of $10^5 \sim 10^6$ pixels. Two or more images taken along different directions are generally needed in order to provide sufficient sampling of the reciprocal space. A simultaneous fit thus involves calculations of $\sim 10^6$ intensity values with perhaps tens of free parameters including force constants, background and intensity normalization parameters, geometrical factors, and sample orientations. Nonetheless, the task for first-order calculations is straightforward and quite manageable on a personal computer.

Fitting, however, has problems. Trapping at a local minimum is one. There are standard numerical methods to minimize such occurrences. Another problem is that the results are only as good as the model. In Nb, for example, it is known that a force constant model needs to include up to about the eighth neighbors in order to describe the phonon dispersion relations accurately. Without such prior knowledge, TDS analysis based on simpler models with fewer neighbors would lead to inferior results. In general, one should perform such analysis for increasing numbers of neighbors until a satisfactory fit is obtained. A large number of fitting parameters, however, tend to increase the chances of spurious solutions and trapping at local minima. The fitting must also take into proper account of background due to scattering from objects near the sample and of intensities derived from higher order TDS, Compton, and defect scattering. These contributions are typically weak and/or relatively featureless, but not always. To minimize higher order TDS scattering and anharmonic effects, it is better to work at low temperatures. A very low sample temperature, however, is not necessarily desirable, as phonons at higher frequencies might not give rise to a sufficiently high scattering intensity for an accurate analysis.

The advantages of TDS measurements are experimental simplicity and a high data acquisition rate. In comparison,
 neutron scattering requires a large sample size, and the data acquisition time is typically much longer. Inelastic X-ray scattering involves much more complicated instrumentation, and measurements are generally slow and limited to one or a few points in reciprocal space at a time. Modern materials of interest often do not come in the form of large single crystals, and many materials of interest exhibit domains that are important to their functions. X-rays can be focused down to micron sizes or even smaller, and the methods based on X-rays are thus much better choices for these cases. The high efficiency of the TDS method can be particularly advantageous for cases requiring a large data set, for example, detailed temperature, pressure, or field dependences near a phase transition. Typical exposure times are seconds, which are not limited by beam intensity but mostly by experimental convenience. Shorter times are quite feasible. It should be fairly easy to ramp through a phase transition and obtain closely spaced data points for critical exponent analysis and for dynamic studies at time scales perhaps as short as 10 ms.

What are likely the developments of TDS in the future? Perhaps the method is most useful for studies of phase transitions. Once the basic phonon structure is known (from TDS or other methods), it is fairly straightforward to carry out an analysis of the TDS intensities in terms of changes in the phonon structure, which is generally a simpler problem than directly inverting TDS patterns to yield an entire set of phonon dispersion curves. Most phase transitions involve a substantial participation of the lattice. Even nominally electronically driven phase transitions are often accompanied by a significant lattice distortion. TDS is thus a useful tool for a broad range of problems and systems. X-ray energies from synchrotron sources are easily tunable. The atomic scattering factor $f_1$ can change drastically near an absorption edge. TDS data taken at different X-ray energies may yield additional information or constraint that aids data analysis.

It would be highly desirable if general and simple methods can be developed for direct inversion of TDS data into phonon dispersion curves without the use of any model or fitting. Ideas have been proposed, including the use of polarization selection rules and special scattering geometries for special points in the Brillouin zone [29, 35]. Most of the methods proposed, however, are subject to errors caused by background and higher-order scattering, especially if absolute scattering intensities are needed as input. First-order scattering is particularly simple as each scattering vector $q$ involves phonons at $q$ only. Higher-order (multi-phonon) scattering can involve all modes in the Brillouin zone. As mentioned above, higher-order calculations involve additional Brillouin-zone sums (or integrals) that are numerically demanding. This becomes a much tougher problem for direct inversion. Operating at a low temperature to minimize higher-order scattering is a possible solution. This also minimizes anharmonic effects, which are ignored in the analysis presented above. Our group is actively pursuing the development of direct-inversion methods.

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