

On model-free reconstruction of lattice dynamics from thermal diffuse scattering

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Expressions are derived for thermal diffuse scattering (TDS) using a formalism based on Born’s S-matrix. It is shown that for monoatomic crystals the dynamical matrix containing the full information on lattice dynamics can be recovered from one-phonon TDS intensities. For any non-monoatomic crystal, part of the information is always lost in the kinematic approximation, but can in principle be recovered by measuring TDS in the dynamical scattering regime. In the long-wave limit the description here coincides with known results.

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1. Introduction

In the following discussion we assume the validity of both (quasi)-harmonic and adiabatic approximations. In this particular case the dynamical matrix, being the Fourier transform of the force matrix, provides the complete phonon dispersion spectrum and thus elastic constants and lattice thermodynamics of the material.

Traditionally experimental information on phonon dispersion is obtained from inelastic neutron (INS) and inelastic X-ray scattering (IXS). In most cases the data are collected point-by-point and branch-by-branch along the high-symmetry directions of the crystal. Consequently typical data-collection times are at least a few days, even with the most advanced spectrometers. From the intensities of inelastic scattering, only limited information on the phonon eigenvectors is available (Strauch & Dorner, 1986). Therefore, for a quantitative analysis of the dispersion relations it is necessary to introduce a model of interatomic interactions (the force matrix) which reproduces the eigenvalues. Alternatively one may compare experiment with *ab initio* calculations.

The distribution of inelastic X-ray scattering by thermally populated phonons in reciprocal space also carries information on phonon dispersion (Lonsdale, 1948). This scattering reduces the intensity of Bragg spots (this reduction is parameterized as Debye–Waller factors in crystal structure analysis) and substantially increases the intensity of the background scattering (Wooster, 1962). Historically phonon dispersion was first determined from thermal diffuse scattering (TDS) (Olmer, 1948); however, the potential of TDS remained largely unexploited and lattice dynamics studies were predominantly conducted using INS and IXS. Recently the advent of third-generation synchrotron sources with their outstanding brilliance has led to a revival of TDS studies (Holt *et al.*, 2001, 2007; Xu & Chiang, 2005). In comparison with traditional methods employing point detectors, the use of area detectors for the collection of TDS patterns has the advantage of a high data-acquisition rate, *i.e.* experimental times range from a few minutes to hours (instead of several days), with a much simpler and therefore more stable experimental set-up. Up to now the extraction of the phonon dispersions from TDS was typically performed using a pre-defined model of interatomic potentials. The present work addresses the question under which conditions a model-free reconstruction of the full lattice dynamics is possible.

2. Theoretical formalism

The intensity of first-order thermal diffuse scattering from a crystal containing N atoms in the unit cell at temperature T and momentum transfer \mathbf{Q} can be written as

$$I(\mathbf{Q}) \propto \sum_{j=1}^{3N} \frac{1}{\omega_j(\mathbf{q})} \coth \left[\frac{\hbar\omega_j(\mathbf{q})}{2kT} \right] \left| \sum_{d=1}^N f_d(\mathbf{Q}) \exp[-W_d(\mathbf{Q}) + i\mathbf{Q} \cdot \mathbf{r}_d] [\mathbf{Q} \cdot \sigma_d^j(\mathbf{q})] M_d^{-1/2} \right|^2, \quad (1)$$

where $\omega_j(\mathbf{q})$ is the frequency of mode j at reduced momentum transfer $\mathbf{q} = \mathbf{Q} - \boldsymbol{\tau}$, σ_d^j is the d -site projected component of the $3N$ -dimensional normalized eigenvector of the phonon mode j defined in periodic notations $\sigma^j(\mathbf{q} + \boldsymbol{\tau}) = \sigma^j(\mathbf{q})$, where $\boldsymbol{\tau}$ is an arbitrary reciprocal lattice vector, $f_d(\mathbf{Q})$ is the atomic scattering factor of atom d with mass M_d and Debye–Waller factor $W_d(\mathbf{Q})$ at the position \mathbf{r}_d , and k is Boltzmann’s constant (Xu & Chiang, 2005). Note that the above expression contains both eigenvalues $\omega_j(\mathbf{q})$ and eigenvectors $\sigma^j(\mathbf{q})$ of the dynamical matrix $D(\mathbf{q})$.

In order to obtain the TDS intensity expressed *via* the dynamical matrix $D(\mathbf{q})$, we first note that

$$|\mathbf{Q} \cdot \sigma^j(\mathbf{q})|^2 = \mathbf{Q}^T \cdot [\sigma^j(\mathbf{q}) \otimes \sigma^j(\mathbf{q})^{*T}] \cdot \mathbf{Q} = \mathbf{Q}^T \cdot P(\mathbf{q}) \cdot \mathbf{Q},$$

where $P(\mathbf{q}) = \sigma^j(\mathbf{q}) \otimes \sigma^j(\mathbf{q})^{*T}$ is the projector matrix; here we redefine the momentum transfer vector in $3N$ -dimensional space merging the three-dimensional \mathbf{Q} N times as

$$\mathbf{Q}^T = (Q_x \quad Q_y \quad Q_z \quad \dots \quad \dots \quad Q_x \quad Q_y \quad Q_z).$$

Equation (1) can therefore be rewritten in the alternative form

$$I(\mathbf{Q}) \propto \mathbf{Q}^T \cdot \sum_{j=1}^{3N} \frac{1}{\omega_j} \coth \left(\frac{\hbar\omega_j}{2kT} \right) Z(\mathbf{Q}) P(\mathbf{q}) Z^*(\mathbf{Q}) \cdot \mathbf{Q}, \quad (2)$$

where the matrix $Z(\mathbf{Q})$ is defined as

$$Z(\mathbf{Q}) = \begin{pmatrix} z_1 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & z_1 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & z_1 & \dots & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & z_N & 0 & 0 \\ 0 & 0 & 0 & \dots & 0 & z_N & 0 \\ 0 & 0 & 0 & \dots & 0 & 0 & z_N \end{pmatrix},$$

where

$$z_d = f_d(\mathbf{Q}) \exp[-W_d(\mathbf{Q}) + i\mathbf{Q} \cdot \mathbf{r}_d] M_d^{-1/2}.$$

Note that the matrix $Z(\mathbf{Q})$ depends on the atomic coordinates and Debye–Waller factors only, and can therefore be obtained from a Bragg diffraction experiment.

Since ω_j^2 are the eigenvalues of the (Hermitian) dynamical matrix $D(\mathbf{q})$, the intensity reads

$$I(\mathbf{Q}) \propto \mathbf{Q}^T \cdot Z(\mathbf{Q}) S(\mathbf{q}) Z^*(\mathbf{Q}) \cdot \mathbf{Q}, \quad (3)$$

where

$$\begin{aligned} S(\mathbf{q}) &= \frac{\hbar}{2[D(\mathbf{q})]^{1/2}} \coth\left(\frac{\hbar[D(\mathbf{q})]^{1/2}}{2kT}\right) \\ &= kT \left[D^{-1}(\mathbf{q}) + \frac{1}{12} \left(\frac{\hbar}{kT}\right)^2 I - \frac{1}{720} \left(\frac{\hbar}{kT}\right)^4 D(\mathbf{q}) + \dots \right] \end{aligned} \quad (4)$$

and I stands for a unit matrix of appropriate size. $D(\mathbf{q})$ and $S(\mathbf{q})$ are linked by a biunique function and therefore the inversion is possible for non-degenerate $D(\mathbf{q})$. The first term in (4) is sufficient for the description if $(\hbar/kT)^2 \|D(\mathbf{q})\| \ll 1$.

Expression (4) defines the so-called S-matrix introduced by Born in 1942 (Born, 1942) and already contained in Waller's dissertation, as Born mentions. The S-matrix decomposition has been applied before for the analysis of Debye–Waller factors (Scheringer, 1972; Groenewegen & Huiszoon, 1972; see also Willis & Pryor, 1975). To the best of our knowledge, this formalism has not been reported in the context of TDS.

For the special case of monoatomic crystals,

$$Z(\mathbf{Q}) = f(\mathbf{Q}) \exp[-W(\mathbf{Q})] \cdot I, \quad (5)$$

$$I(\mathbf{Q}) \propto f^2(\mathbf{Q}) \exp[-2W(\mathbf{Q})] \cdot \mathbf{Q}^T \cdot S(\mathbf{q}) \cdot \mathbf{Q}. \quad (6)$$

As $S(\mathbf{q})$ and $D(\mathbf{q})$ for a monoatomic crystal are real and symmetric, the minimum \mathbf{Q} -set for a complete $D(\mathbf{q})$ reconstruction at arbitrary \mathbf{q} assumes six observations at most. The rank of the system of equations to be solved has to be six for a general point. Reciprocal-space mapping with a two-dimensional detector allows over-determination for the system of equations (6) for any \mathbf{q} , thus providing the phonon dispersion, density of states and all the derived values. Lorentz and polarization corrections have to be applied prior to the treatment.

For non-monoatomic crystals, $S(\mathbf{q})$ at an arbitrary \mathbf{q} remains just Hermitian even if the dynamical matrix takes a special shape (*i.e.* if every atom sits at a center of inversion). At no value of τ do the imaginary parts of the non-diagonal elements of the 3×3 blocks situated on the diagonal of the S-matrix, $\text{Im}[S_{\alpha\beta}(dd|\mathbf{q})]$ ($\alpha \neq \beta$), give any contribution to the final intensity as the corresponding terms [see equation (3)] are equal to

$$Q_\alpha Q_\beta z_d [S_{\alpha\beta}(dd|\mathbf{q}) + S_{\beta\alpha}(dd|\mathbf{q})] z_d^* = 2Q_\alpha Q_\beta \text{Re}[S_{\alpha\beta}(dd|\mathbf{q})] |z_d|^2.$$

Therefore neither $S(\mathbf{q})$ nor $D(\mathbf{q})$ can be completely reconstructed from TDS data only. $3N$ values of the complex matrix $S(\mathbf{q})$ are irreversibly lost in a kinematic scattering experiment; this statement holds true for simple structures like NaCl or diamond. The number of lost parameters might reduce for a limited set of \mathbf{q} vectors where

$\text{Im}[S_{\alpha\beta}(dd|\mathbf{q})] = 0$, presumably situated at the center and boundary of the Brillouin zone. For compounds with more than one atom per unit cell, TDS may be used for the validation of theoretical models, as are phonon dispersions, and thus provide valuable information on the validity of the model.

Information on the missing elements of the S-matrix may be recovered from coherent X-ray scattering. Coherently coupled beams can be prepared by dynamical diffraction methods (Kohl, 1985; Spalt *et al.*, 1988): when a Bragg spot with momentum transfer \mathbf{G} is excited and the ratio of electric field amplitudes of the diffracted and incident beams is α , the intensity can be written as

$$I(\mathbf{Q}, \mathbf{G}) = I(\mathbf{Q}) + |\alpha|^2 I(\mathbf{Q} - \mathbf{G}) + I_{\text{coh}}. \quad (7)$$

Here the interference term I_{coh} is due to the coherence of incident and diffracted beams and reads

$$I_{\text{coh}} \propto \text{Re}[\alpha \mathbf{Q}^T \cdot Z(\mathbf{Q}) S(\mathbf{q}) Z^*(\mathbf{Q} - \mathbf{G}) \cdot (\mathbf{Q} - \mathbf{G})]. \quad (8)$$

Now $\text{Im}[S_{\alpha\beta}(dd|\mathbf{q})]$ does contribute to the final intensity and the complete lattice dynamics can in principle be reconstructed, though this approach is neither easy nor very practical.

Some use of the above formalism can also be made in the long-wave limit, where the dominating scattering comes from acoustic phonons with the linear dispersion $\omega \propto qV$ ($q = |\mathbf{q}|$, V is the sound velocity). Under this condition, expressions (1) and (3) can be reformulated as follows,

$$I \propto |F(\mathbf{Q})|^2 \mathbf{Q}^T \cdot \sum_{j=1}^3 \frac{1}{qV_j} \coth\left(\frac{\hbar q V_j}{2kT}\right) P(\mathbf{q}) \cdot \mathbf{Q}, \quad (9)$$

where we use the standard form of the structure factor

$$F(\mathbf{Q}) = \sum_{d=1}^N f_d(\mathbf{Q}) \exp[-W_d(\mathbf{Q}) + i\mathbf{Q} \cdot \mathbf{r}_d]$$

and $P(\mathbf{q})$ is defined *via* sound-wave polarizations. Using Christoffel's equation with $\Lambda_{jk}(\mathbf{q}) = [1/(\rho q^2)] C_{ijkl} q_i q_l$, we obtain

$$I \propto |F(\mathbf{Q})|^2 \mathbf{Q}^T \cdot S'(\mathbf{q}) \cdot \mathbf{Q}, \quad (10)$$

where

$$S'(\mathbf{q}) = \frac{\hbar}{2q[\Lambda(\mathbf{q})]^{1/2}} \coth\left\{\frac{\hbar q[\Lambda(\mathbf{q})]^{1/2}}{2kT}\right\}. \quad (11)$$

Since in the long-wave limit $kT \gg \hbar q |\Lambda|^{1/2}$ is easily fulfilled, equation (11) can be reduced to

$$S'(\mathbf{q}) = \frac{kT}{\hbar q^2} \Lambda^{-1}(\mathbf{q}),$$

and previously established results are thus recovered (Wooster, 1962). Collecting data in all directions for multiple Γ -points (Bragg nodes) allows the complete reconstruction of $\Lambda(\mathbf{q})$ (independent of q), and therefore the determination of the full set of elastic moduli from a simple diffraction experiment.

3. Conclusions

We have derived expressions for thermal diffuse scattering using Born's S-matrix formalism. This formalism proves immediately that the complete information on lattice dynamics in terms of the dynamical matrix can only be recovered from one-phonon TDS intensities for a monoatomic crystal. For more complex structures, part of the information is irreversibly lost in the kinematic scattering regime, but can in principle be recovered by measuring TDS in the dynamical scattering regime. However, even for the kinematic scattering case, a

complete reconstruction is still possible for a limited number of points in the Brillouin zone.

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References

- Born, M. (1942). *Rep. Prog. Phys.* **9**, 294–333.
Groenewegen, P. P. M. & Huiszoon, C. (1972). *Acta Cryst.* **A28**, 166–169.
Holt, M., Sutton, M., Zschack, P., Hong, H. & Chiang, T.-C. (2007). *Phys. Rev. Lett.* **98**, 065501.
Holt, M., Zschack, P., Hong, H., Chou, M. Y. & Chiang, T.-C. (2001). *Phys. Rev. Lett.* **86**, 3799–3802.
Kohl, H. (1985). *Phys. Status Solidi B*, **130**, 151–159.
Lonsdale, K. (1948). *Crystals and X-rays*. London: G. Bell.
Olmer, P. (1948). *Acta Cryst.* **1**, 57–63.
Scheringer, C. (1972). *Acta Cryst.* **A28**, 512–515.
Spalt, H., Dev, B. N. & Materlik, G. (1988). *Phys. Rev. Lett.* **60**, 1868–1871.
Strauch, D. & Dorner, B. (1986). *J. Phys. C*, **19**, 2853–2864.
Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.
Wooster, W. A. (1962). *Diffuse X-ray Reflections from Crystals*. Oxford: Clarendon.
Xu, R. & Chiang, C. (2005). *Z. Kristallogr.* **220**, 1009–1016.