Low-frequency lattice vibrations from atomic displacement parameters of \(\alpha\)-FOX-7, a high energy density material

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Highly anharmonic thermal vibrations may serve as a source of structural instabilities resulting in phase transitions, chemical reactions and even the mechanical disintegration of a material. \textit{Ab initio} calculations model thermal motion within a harmonic or sometimes quasi-harmonic approximation and must be complimented by experimental data on temperature-dependent vibrational frequencies. Here multi-temperature atomic displacement parameters (ADPs), derived from a single-crystal synchrotron diffraction experiment, are used to characterize low-frequency lattice vibrations in the \(\alpha\)-FOX-7 layered structure. It is shown that despite the limited quality of the data, the extracted frequencies are reasonably close to those derived from inelastic scattering, Raman measurements and density functional theory (DFT) calculations. Vibrational anharmonicity is parameterized by the Grüneisen parameters, which are found to be very different for in-layer and out-of-layer vibrations.

1. Introduction

FOX-7 (DADNE, \(\text{C}_2\text{H}_4\text{N}_4\text{O}_4\)) (Latypov \textit{et al.}, 1998; Trzciński & Belaada, 2016) is a high energy density material (HEDM) that shows a set of phase transformations as a function of temperature and/or pressure (Bu \textit{et al.}, 2020). The structural and mechanical stability of different polymorphs are defined, among other factors, by their thermal molecular vibrations. The structures of all reported crystalline forms of \(\alpha\)-, \(\beta\)- and \(\gamma\)-FOX-7 are built from wave-shaped layers of FOX-7 molecules linked by hydrogen bonding and the stacked layers are weakly bound by van der Waals interactions (Crawford \textit{et al.}, 2007).

The mechanisms for the impact-induced initiation of HEDMs has been debated for many decades. Understanding the initiation process is essential for designing safe and well-performing materials suitable for use across military and civilian applications. Building on early numerical models (Tokmakoff \textit{et al.}, 1993), recent theoretical developments have suggested that initiation is strongly correlated to the dynamic behaviour of the material (Michalchuk \textit{et al.}, 2019, 2021a). When struck by a mechanical force, the energy is inserted into the lattice vibrations, up-converting through phonon–phonon collisions until the molecules are vibrationally excited. If sufficiently excited, covalent-bond rupture occurs, leading to the primary initiation event. These so-called ‘phonon up-pumping’ models have proved to be very promising across a wide range of HEDMs, though their further development...
requires detailed investigations into the structural dynamics of these materials. In connection with this, FOX-7 is of particular interest, owing to its polymorphic behaviour and layered crystal packing, the latter widely believed to indicate insensitivity to impact initiation (Ma et al., 2014). Recent studies have suggested that FOX-7 may undergo a polymorphic transformation in response to mechanical impact (Michaľchuk et al., 2021b), although the influence of such transformations on material performance is not known. Within the framework of phonon up-pumping, a thorough understanding of FOX-7 dynamics is needed before its complex initiation behaviour can be further elucidated.

The use of neutron or X-ray inelastic scattering for studying vibrational properties is rather limited for FOX-7 due to the low molecular symmetry and high lattice anharmonicity, and hence relatively large crystals of FOX-7 are required. This is why only phonon density of states measured with neutron inelastic scattering from powders have been reported so far (Hunter et al., 2015; Michaľchuk et al., 2019). Moreover, the presence of H atoms represents a problem for coherent neutron scattering experiments. Raman and IR spectroscopies provide information on the vibrational frequencies at the Γ-point of the Brillouin zone and are typically restricted to the analysis of wavenumbers > 50–100 cm⁻¹; data on low-frequency vibrations and dispersion are very limited. The majority of spectroscopic techniques are focused on vibrational frequencies (eigenvalues of the dynamical matrices), while phonon eigenvectors are characterized experimentally for very few structurally simple materials (Strauch & Dörner, 1986; Pawley et al., 1980). Here we have applied a concurrent analysis of the variable-temperature ADPs routinely derived from diffraction experiment (Bürgi & Capelli, 2000) to investigate the lattice vibration properties of the monoclinic α-phase of FOX-7. This approach considers eigenvectors of dynamical matrices, which are encoded in the shape of displacement ellipsoids – smearing of atoms in the diffraction experiment. The phonon modes are modelled with line spectra as Einstein oscillators. For a molecular material, thermal vibrations are split on the rigid unit modes (RUMs) – displacements of a molecule as a whole (translations and librations), and deformations associated with optic phonons that normally have higher frequencies. While this approximation is appropriate for all molecular solids, particularly where ‘soft’ molecular modes exist, such as –NO₂ wags, it holds well for crystalline FOX-7 (Michaľchuk et al., 2021a,b).

The monoclinic α-phase of FOX-7 is stable below 380 K. Thus far, only one set of single-crystal X-ray (Mo Kα) diffraction data containing five temperature points in the range 200–293 K at ambient pressure, to d_min of 0.76 Å, is available (Evers et al., 2006). Additional powder data at 403 and 423 K have also been collected, indicating the first-order α→β phase transition (monoclinic P2₁/n → orthorhombic P2₁2₁2₁) at 389 K (Evers et al., 2006). The out-of-plane displacements of four O atoms in two –NO₂ groups are clearly observed in both phases of FOX-7 in the range 200–423 K (Evers et al., 2006). More attention has been paid to FOX-7 under high pressure–temperature conditions, combining experiment and simulation to study its phase transitions, structural changes and vibrational behaviour (Peiris et al., 2004; Hu et al., 2006; Bishop et al., 2012; Dreger et al., 2013, 2014; Appalakondaiah et al., 2014; Hunter et al., 2015). Here we complement the available information on thermal vibrations with low-energy frequencies (librations and translations) and their anharmonic behaviour parameterized with Grüneisen parameters. We also include in the analysis some of the vibrations associated with deformation of the FOX-7 molecule, providing results that are reasonably close to the reported values for low-frequency optic phonons at the Γ-point of the Brillouin zone, as expected for the phonon modes with low dispersion.

The collection of diffraction data with synchrotron light can be easily done with very small crystals; high intensity and fast detectors reduce the data collection time to tens of seconds and the data can be collected with very fine temperature sampling. However, the data quality frequently suffers from a nonhomogeneous and/or unstable beam, an irregular shape of the crystal or inadequately characterized attenuation of the incoming and scattered beams with crystal mounts; all these effects are believed to be minimized with empirical absorption and scaling corrections. ADPs are the most sensitive parameters and may therefore contain an additional contribution not related to thermal smearing but rather linked to the data and data processing, as demonstrated by the simultaneous analysis of multi-temperature ADPs of the three glycine polymorphs (Aree & Bürgi, 2012; Aree et al., 2013, 2014). Here we show that those contributions, being temperature independent, do not distort information on the low-energy thermal vibrations. To improve information concerning the dynamics of H atoms and general quality of ADPs, we have applied a nonspherical refinement of X-ray diffraction data developed by Kleemiss et al. (2021). Altogether, the data collection, data processing and structure refinement applied here show that a vibrational analysis similar to that presented here might become a relatively simple-to-use tool that offers unique information and can be easily implemented for single-crystal diffraction experiments at synchrotron beamlines.

2. Experimental
2.1. Materials

For the synthesis of 1,1-diamino-2,2-dinitroethene (DADNE or FOX-7), 2-methylpyrimidine-4,6-dione (3.0 g, 0.025 mol) was dissolved in H₂SO₄ (95%, 25 ml) at temperatures < 303 K. HNO₃ (99%, 10 ml) was added dropwise, ensuring that the temperature remained below 293 K during addition. The sample was stirred on ice for 3 h. The remaining material was rinsed with H₂SO₄ (95%) and dissolved in deionized water. The precipitated product was filtered off and dried. Single crystals of FOX-7 were grown by slow evaporation from dimethyl sulfoxide (DMSO).
2.2. Multi-temperature single-crystal X-ray diffraction

2.2.1. Synchrotron diffraction experiment. A single crystal of \(\alpha\)-FOX-7 (0.2 x 0.1 x 0.1 mm) was selected and mounted on the tip of a glass fibre with the minimum of high-temperature epoxy. Variable-temperature single-crystal diffraction data were collected at the Swiss–Norwegian Beamline BM01 (ESRF, Grenoble) (Dyadkin et al., 2016) upon heating from 80 to 360 K, with temperature control by an Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986). Fifty eight temperature data points with a 4–8 K increment were

Table 1

| Temp (K) | No. of reflections [all, >2\(\sigma(I)\)] | \(R_1(F)\)* | \(R_1(F)\)* | \(\Delta\rho\) XL (\(\text{e Å}^{-3}\)) | \(\Delta\rho\) NoSpherA2 (\(\text{e Å}^{-3}\)) |
|----------|----------------------------------------|--------------|--------------|--------------------------------|--------------------------------|
| 80       | 1536, 1414                             | 0.0364       | 0.0267       | -0.400                         | 0.256                         |
| 100      | 1536, 1400                             | 0.0368       | 0.0261       | -0.335                         | 0.216                         |
| 120      | 1539, 1394                             | 0.0381       | 0.0279       | -0.340                         | 0.213                         |
| 140      | 1540, 1389                             | 0.0401       | 0.0299       | -0.331                         | 0.227                         |
| 164      | 1542, 1375                             | 0.0409       | 0.0309       | -0.339                         | 0.228                         |
| 200      | 1560, 1363                             | 0.0435       | 0.0334       | -0.304                         | 0.180                         |
| 240      | 1577, 1340                             | 0.0502       | 0.0387       | -0.386                         | 0.207                         |
| 280      | 1576, 1222                             | 0.0692       | 0.0574       | -0.452                         | 0.486                         |
| 320      | 1592, 1124                             | 0.0849       | 0.0774       | -0.472                         | 0.709                         |
| 360      | 1607, 1029                             | 0.0995       | 0.0949       | -0.504                         | 0.681                         |

Note: (a) \(R_1(F) = \Sigma |F_o| - |F_c||/\Sigma |F_o|\).

2.2.2. Intra- and intermolecular O—H—O hydrogen bonds stabilizing the layer-type structure of \(\alpha\)-FOX-7 at 80 K (magenta connecting lines). Note that atoms O21 and O22 having fewer interactions are oriented out of the mean molecular plane.
collected. For each temperature, a full data collection was carried out at a wavelength of 0.62379 Å (19.876 keV) with a single ω-scan. Moreover, multi-temperature data were continuously collected to 474 K and the data between 274 and 474 K were used for an investigation of the thermal expansion and phase transitions of the energetic material FOX-7 (McMonagle et al., 2022). This work shared data between 80 and 360 K for the normal mode analysis.

2.2.2. Data processing. The data were processed with CrysAlis PRO (Rigaku OD, 2016) and the structures were refined with SHELXL (Sheldrick, 2015) in a sequential manner as described in Chernyshov et al. (2019) and Bogdanov et al. (2021). After inspecting the temperature-dependent ADPs of α-FOX-7 and removing the outliers, we decided to use 10 temperature points with 20–40 K steps, which adequately define the continuous smooth ADP curves in the range 80–360 K for the normal mode analysis. OLEX2 (Dolomanov et al., 2009; Bourhis et al., 2015) was then used for the refinement with nonspherical scattering functions (Kleinmisc et al., 2021). Note that in the range 80–360 K, the diffraction θ_{\text{max}} and θ_{\text{max}} values of 23.49 and 32.72–32.97° yield respective data coverages of 89.3–90.9 and 66.0–67.3%. Although the data extended to sin θ/λ ≈ 0.8, the 1σ ratios in the outer shells were rather poor, in particular at T > 280 K (Table 1).

![Graph](image)

Figure 2
Unit-cell parameters of α-FOX-7 in the temperature range 80–360 K.

2.2.3. Simulation of Γ-point α-FOX-7 unit cell. Periodic plane-wave density functional theory (DFT) simulations were performed in CASTEP (Version 20.11; Clark et al., 2005). The electronic structure was expanded in plane waves to a kinetic energy cut-off of 1200 eV, with a charge–density cut-off of 35.49 Å⁻¹. The exchange correlation functional of Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996) was used, alongside the semi-empirical dispersion correction of Tkatchenko–Scheffler (TS) (Tkatchenko & Scheffler, 2009). The electronic wavefunction was accepted following convergence < 10⁻¹⁵ eV and the residual forces converged < 10⁻⁴ eV per atom. Γ-point frequencies and eigenvectors were simulated through the linear response method (Refson et al., 2006), without explicit consideration for LO–TO splitting. Dynamical matrices were subsequently calculated on a 3 × 3 × 3 Monkhorst–Pack grid (Monkhorst & Pack, 1976), and interpolated onto a 9 × 9 × 9 fine grid, with which the ADPs were calculated as implemented within the CASTEP suite.

2.2.4. DFT calculations of internal vibrational frequencies. The atomic coordinates of α-FOX-7 at 80 K were employed to estimate internal vibrational frequencies. The structure was initially optimized with the semi-empirical PM3 method and was then fully re-optimized using DFT calculations in the gas phase at the B3LYP/6-311+G(2d,p) level of theory with the program GAUSSIAN09 (Frisch et al., 2009). The energy minimization converged smoothly to a global minimum. After scaling, the harmonic vibrational frequencies in the range 57–3546 cm⁻¹ agree with the literature data (see §3.3).

3. Results and discussion

3.1. Crystal structure of α-FOX-7

There are four α-FOX-7 molecules in the monoclinic unit cell with the space group P2₁/n [Fig. 1(b)]. The α-FOX-7 molecule is nonplanar, as indicated by the larger deviations (Å) of atoms from the mean molecular plane: O11—0.209 (1), O21—0.441 (1) and O22 0.761 (1), and the greater variations (~3°–9°) of the C2—C1—N11(N12)—O11(O21/O22) torsion angles from planarity for the 80 K data [Figs. 1(a) and 1(b)]. This is due to the steric hindrance between the two nitro groups and the small number of hydrogen-bonding interactions [Fig. 1(d)]. In the crystal, adjacent α-FOX-7 molecules are closely connected via N—H···O hydrogen bonds along the c axis, forming herringbone layers with an obtuse interplanar angle of 140.10 (2)° [Fig. 1(c)]. These layers are loosely packed along the b axis, allowing greater changes on this axis, as observed from the unit-cell volume expansion with increasing temperature (Fig. 2) and from the unit-cell volume contraction at high pressure (Hunter et al., 2015).

3.2. Multi-temperature ADPs of α-FOX-7

The multi-temperature ADPs of α-FOX-7 behave as expected within the harmonic approximation; see the principal elements U₁₁, U₂₂ and U₃₃ for atoms C1, N21 and O11 [Figs. 3(a), 3(b) and 3(c), respectively]. In the classical regime, the ADPs increase linearly with temperature (80–164 K), but
begin to increase more steeply at higher temperatures, thereby indicating marked lattice anharmonicity in α-FOX-7. This anharmonicity is captured by the Grüneisen parameter (see §3.4). As the α-FOX-7 data do not cover the quantum regime (low temperature-independent limit), the theoretically temperature-independent ADPs, observed in the glycine polymorphs (Aree et al., 2014), are not noticed here. Note that the elements $U_{11}$ of all atoms increase more slowly at $T > 300$ K, resulting in an intersection of the curves $U_{11}$ and $U_{33}$. This is probably due to the approach of the α-to-β phase transition at 389 K (Evers et al., 2006), although the unit-cell parameters of α-FOX-7 do not show a discontinuity at the temperature of the present experiment (Fig. 2). The data resolution is not sufficient to really see the effects of bonding, so that the more elaborate charge–density description (NoSpherA2) does not have a large effect on the overall fit; see the ADP curves with open symbols in Figs. 3(a), 3(b) and 3(c). The $R_1$ values are improved by 0.0046–0.0118 and the magnitudes of the highest peaks and deepest holes are decreased by 0.029–0.265 and 0.004–0.171 e Å$^2$, respectively (Table 1).

We attempted to reproduce the variable-temperature ADPs of α-FOX-7 using periodic DFT simulations at the PBE-TS level of theory (Fig. 4). At the fully optimized geometry (i.e. the 0 K structure), our simulated harmonic ADPs consistently underestimate the magnitude of the primary displacement vectors, even at 100 K. This effect is, however, relatively small for both $U_{22}$ and $U_{33}$. This indicates a significant degree of anharmonicity in the FOX-7 structure, particularly in the direction between herringbone chains. Within the harmonic model, the mean-square atomic displacement increases approximately linearly with temperature. Thus, the growing deviation between our simulation from experiment with

![Graph showing ADPs](image)

**Figure 4**
The average absolute deviations of ADPs for each atom type in α-FOX-7, with $\Delta U = \frac{1}{2} \sum_i [U_{i}(\text{exp}) - U_{i}(\text{calc})]$ for the $i$ atoms of each type. Values are shown as absolute deviations between the ADPs from the harmonic simulation and the diffraction experiment at each temperature.

![Graph showing multi-temperature ADPs](image)

**Figure 3**
Multi-temperature ADPs of α-FOX-7 for atoms (a) C1, (b) N21 and (c) O11 from XL and NoSpherA2 refinements. The standard uncertainties are $3 \times 10^{-4}$ Å$^2$, or $\sigma$ the line thickness. The displacement ellipsoid plot (50% probability level) with atom numbering is shown for α-FOX-7 at 80 K.
Table 2
Comparison of internal vibrational frequencies (cm⁻¹) of α-FOX-7 from calculations and Raman measurement.

| DFT⁵ | MP² | p-DFT⁴ | p-DFT⁴ | Exp.⁴ | Assignment⁵ |
|------|-----|--------|--------|-------|-------------|
| 57   | 119 | 123    |        |       | NO₂ twist   |
| 92   | 151 | 194    |        |       | NO₂ twist   |
| 115  | 193 | 233    |        | 246   | C—NH₂ wag   |
| 203  | 270 | 253    |        | 318   | NO₂ rock, NH₂ wag |
| 299  | 317 | 316    |        |       | NO₂ rock, NH₂ twist |
| 320  | 324 | 331    |        |       | NH₂, NO₂ rock |
| 369  | 378 | 397    |        | 400   | NH₂ rock   |
| 378  | 441 | 444    |        | 457   | NH₂, NO₂ rock |
| 432  | 443 | 477    |        | 472   | NH₂ rock, NO₂ twist, C—C st |
| 454  | 469 | 490    |        | 481   | NH₂ twist, C—C st, NO₂ sci |
| 454  | 598 | 634    |        |       | NH₂ twist |
| 454  | 610 | 646    |        |       | NH₂ wag |
| 590  | 633 | 676    |        | 622   | NH₂ sci, twist |
| 605  | 658 | 681    |        |       | NH₂ twist |
| 666  | 668 | 695    |        |       | NH₂ wag |
| 704  | 715 | 723    |        |       | C—NO₂ umb, NH₂ twist |
| 732  | 735 | 741    |        | 737   | C—NO₂ umb, NH₂ twist |
| 735  | 766 | 775    |        | 749   | NH₂ rock, NO₂ sci |
| 783  | 797 | 821    |        | 789   | NH₂ twist |
| 841  | 833 | 843    |        | 856   | NO₂ sci, C—C st, NH₂ rock |
| 1041 | 1006| 1063   |        | 1024  | NH₂ rock |
| 1049 | 1050| 1084   |        | 1070  | NH₂ rock |
| 1106 | 1106| 1119   |        | 1142  | NH₂ rock, NO₂ st (sym) |
| 1120 | 1141| 1156   |        | 1165  | NH₂ rock, C—C st |
| 1220 | 1190| 1201   |        | 1208  | C—NO₂ st (asym), NH₂ sci |
| 1287 | 1300| 1315   |        | 1311  | C—NO₂ st (sym), NH₂ rock |
| 1403 | 1321| 1339   |        | 1343  | NH₂ sci, NO₂ st (asym) |
| 1471 | 1398| 1411   |        | 1386  | NH₂ rock, C—C st, NO₂ st (asym) |
| 1505 | 1480| 1493   |        | 1506  | NH₂ sci, C—C st |
| 1530 | 1497| 1519   |        | 1528  | NH₂ sci, C—C rock |
| 1560 | 1562| 1599   |        | 1606  | NH₂ sci, C—C st |
| 1581 | 1603| 1624   |        | 1630  | NH₂ sci, C—C rock |
| 3341 | 3288| 3293   |        | 3299  | NH₂ st (sym) |
| 3354 | 3321| 3334   |        | 3333  | NH₂ st (sym) |
| 3544 | 3418| 3424   |        | 3405  | NH₂ st (sym) |
| 3546 | 3433| 3450   |        | 3425  | NH₂ st (sym) |

Notes: (a) DFT/B3LYP/6-311+G(2d,p) calculation in a vacuum; frequencies are scaled by a factor of 0.965 (this work). (b) MP2/6-31G(d,p) calculation in a vacuum; frequencies are scaled by a factor of 0.937 (Sorescu et al., 2001). (c) Periodic-DFT (p-DFT) calculation (Clark et al., 2005). (d) Raman measurement from solid sample with vibrational assignment: twist = twisting, wag = wagging, rock = rocking, scissor = scissoring, umb = umbrella, st = stretching, sym = symmetric and asym = asymmetric (Dreger et al., 2014).
deformations of NO₂ and CN₂ groups (U₁, U₂ and U₃) to rbeg.

(iii) Model rbeg+3b+1f further includes one temperature-independent high frequency, which is attributed to CN₂ wagging and NO₂ twisting. The molecular orientation is set as follows: the x axis passing through the N22→O11 vector is completed with a right-hand rule by the y axis going through the N21→O22 vector (Fig. 5). The results of normal mode analysis are summarized in Table 3. The lattice vibrational frequencies from ADP analysis are compared to those derived from other techniques in Table 4. The model of motion rbeg+3b+1f provides estimated ADPs in fair agreement with the ADPs from diffraction, as depicted with the quite random

| Table 3 | Normal mode analysis of multi-temperature ADPs of α-FOX-7. |
|---------|---------------------------------------------------------|
| Frequency (cm⁻¹) and eigenvector | Grüniesen | ε (× 10⁻⁴)ᵃᵇ | GOF⁻ | wR₂ (%)ᵈ |
| ADP_NoSph; Model rbeg+3b+1f | | |
| 85.2 (48) | 76.5 (46) | 97.5 (29) | 2.5 (2) | 2.5 (2) | 3.19 | 9.30 |
| 44.6 (6) | 56.6 (11) | 39.4 (5) | 2.5 (2) | 9 (3) | 0 (1) | 3 (1) | 25 (3) | Observations: 840 |
| 145.5 (32) | | | | | | |
| L₁ | -0.607 (641) | 0.702 (524) | -0.011 (105) | | | |
| L₂ | -0.317 (145) | 0.054 (356) | 0.306 (57) | | | |
| L₃ | -0.060 (120) | 0.070 (75) | -0.947 (14) | | | |
| T₁ | -0.739 (14) | -0.624 (14) | 0.253 (22) | | | |
| T₂ | 0.667 (14) | -0.731 (12) | 0.143 (22) | | | |
| T₃ | 0.996 (26) | 0.274 (14) | 0.957 (5) | | | |
| U₁ | -0.407 (565) | -0.062 (337) | 0.034 (57) | | | |
| U₂ | 0.492 (473) | 0.075 (307) | 0.041 (63) | | | |
| U₃ | 0.345 (90) | 0.042 (610) | 0.080 (59) | | | |

ADP_NoSph; Model rbeg+3b | | |
| 93.5 (26) | 64.7 (27) | 97.7 (58) | 2.4 (2) | 2.4 (2) | 3.16 | 9.19 |
| 44.5 (6) | 56.2 (10) | 39.5 (5) | | | |

ADP_NoSph; Model rbeg+3b [free 6 Grün.] | | |
| 98.8 (41) | 62.1 (13) | 113.6 (64) | 2.50 | 7.23 |
| 4.3 (8) | 2.8 (4) | 4.5 (10) | 840/45/78 |
| 44.1 (63) | 71.0 (17) | 38.3 (5) | |
| 0.7 (4) | 8.3 (5) | 1.1 (3) | |

ADP_NoSph; Model rbeg | | |
| 64.3 (16) | 87.1 (33) | 92.6 (51) | 2.1 (4) | 2.1 (4) | 6.24 | 18.4 |
| 45.2 (12) | 57.6 (24) | 38.0 (9) | | | |

ADP_XL; Model rbeg | | |
| 57.3 (12) | 79.0 (24) | 99.9 (61) | 2.3 (5) | | |
| 43.9 (12) | 55.0 (20) | 42.2 (11) | 2.3 (5) | 5.06 | 15.2 |
| 640/50/60 |

Notes: (a) the H-atom epsilons are restrained to the values from DFT calculations. (b) The diagonal elements of epsilon for non-H atoms from DFT calculations are 13, 19, 13 × 10⁻¹ Å². (c) Goodness-of-fit (GOF) based on numbers of observations (OBS), restraints (Restr) and parameters (Param). (d) wR₂ = [Σw(U_{obs} - U_{calc})²/ΣwU_{obs}²]¹/².

Figure 5
PEANUT plots showing the difference displacement parameters 3 × (U_{obs} - U_{calc}) of α-FOX-7 from synchrotron diffraction (80–360 K); positive and negative differences are shown with respective solid and dashed lines. Axes shown are the molecular coordinate system for normal mode analysis; see text for more details. The r.m.s. values of Σ(U/σ_{obs}) = 3–4 for non-H and ~1 for H atoms.
9.30%. The six lattice vibrational frequencies (translations: \(T_x\), \(T_y\), \(T_z\)) are obtained from bending, wagging and twisting of NO2 and CN2 significantly improved by the addition of the deformations of NO2 and CN2 groups, and one temperature-independent ADPs (Table 3). The model of motion, a Gruneisen constant, two epsilons (the temperature-dependent ADPs for H and non-H atoms), three bending deformations of NO2 and CN2 groups, and one temperature-independent high frequency (attributed to CN2 wagging and NO2 twisting). The anharmonicity arising from in-layer and out-of-layer vibrations is parameterized by the distinct Gruneisen parameters. In addition, we demonstrate that despite the limited quality of the diffraction data, the lattice vibrational frequencies from ADP analysis are reasonably close to those derived from inelastic scattering, Raman measurements and DFT calculations.

We conclude with a general note on experimentation. Single-crystal data collection with bright synchrotron radiation is fast, but complete and highly redundant ‘multi-run’ high-resolution data may allow sufficient time to see the effects associated with beam instabilities and radiation damage. Single-run data acquisitions, like those used here, rapidly map the temperature evolution of a crystal structure but suffer from reduced completeness and redundancy. With the example of vibrational analysis based on temperature-dependent ADPs, we show that the useful and sometimes unique information content does not suffer from such a compromise.

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References

Appalakondaiah, S., Vaitheeswaran, G. & Lebègue, S. (2014). *J. Chem. Phys.* **140**, 014105.

Arec, T., Bürgi, H. & Capelli, S. C. (2012). *J. Phys. Chem. A* **116**, 8092–8099.

Arec, T., Bürgi, H., Chernyshov, D. & Törnroos, K. W. (2014). *J. Phys. Chem. A* **118**, 9951–9959.

Arec, T., Bürgi, H., Minkov, V. S., Boldyrev, E. V., Chernyshov, D. & Törnroos, K. W. (2013). *J. Phys. Chem. A* **117**, 8001–8009.

Averkiev, B. B., Dreger, Z. A. & Chaudhuri, S. (2014). *J. Phys. Chem. A* **118**, 10002–10010.

Bishop, M. M., Chellappa, R. S., Pravica, M., Coe, J., Liu, Z., Dattlebaum, D., Vohra, Y. & Velisavljevic, N. (2012). *J. Chem. Phys.* **137**, 174304.

Bogdanov, N. E., Zakharov, B. A., Chernyshov, D., Pattison, P. & Boldyrev, E. V. (2015). Acta Crystallography Section B **B77**, 365–370.

Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *Acta Crystallography Section A* **A65**, 403–412.

Boukhit, H., Hauser, J. & Bürgi, H. B. (1990). *Chem. Phys.* **150**, 4996–5007.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Crawford, M. J., Evers, J., Göbel, M., Klapötke, T., Mayer, P., Oehlinger, G. & Welch, J. (2007). *Prop. Explo. Pyrotech.* **32**, 478–495.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Dreger, Z. A., Tao, Y. & Gupta, Y. M. (2013). *Chem. Phys. Lett.* **527–544, 584**, 83–87.

Dreger, Z. A., Tao, Y. & Gupta, Y. M. (2014). *J. Phys. Chem. A* **118**, 5002–5012.

Dyadkin, V., Pattison, P., Dmitriev, V. & Chernyshov, D. (2016). *J. Synchrotron Rad.* **23**, 825–829.

Evers, J., Klapötke, T. M., Mayer, P., Oehlinger, G. & Welch, J. (2006). *Inorg. Chem.* **45**, 4996–5007.

Frisch, M. J. et al. (2009). *GAUSSIAN09*, Revision A.01. Gaussian Inc., Wallingford, CT, USA. https://gaussian.com/.

Hu, A., Larade, B., Abou-Rachid, H., Lussier, L. S. & Guo, H. (2006). *Prop. Explo. Pyrotech.* **31**, 355–360.

Hummel, W., Hauser, J. & Bürgi, H. B. (1990). *J. Mol. Graph.* **8**, 214–220.

Hunter, S., Coster, P. L., Davidson, A. J., Millar, D. I., Parker, S. F., Marshall, W. G. & Pulham, C. R. (2015). *J. Phys. Chem. C**119**, 2322–2334.

Kleemiss, F., Dolomanov, O. V., Bodenstein, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauser, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021). *Chem. Sci.* **12**, 1675–1692.

Latypov, N. V., Bergman, J., Langetl, A., Wellmar, U. & Bemm, U. (1998). *Tetrahedron* **54**, 11525–11536.

Ma, Y., Zhang, A., Xue, X., Jiang, D., Zhu, Y. & Zhang, C. (2014). *Cryst. Growth Des.* **14**, 6101–6114.

McMonagle, C. J., Michalchuk, A. A. L. & Chernyshov, D. (2022). *Acta Crystallographica Section B* **B78**, 91–95.

Michalchuk, A. A. L., Trestman, M., Rudič, S., Portius, P., Fincham, P. T., Pulham, C. R. & Morrison, C. A. (2021b). *Chem. Commun.* **57**, 11213–11216.

Michalchuk, A. A. L., Trestman, M., Rudič, S., Portius, P., Fincham, P. T., Pulham, C. R. & Morrison, C. A. (2019). *J. Mater. Chem. A* **7**, 19539–19553.

Monkhorst, H. J. & Pack, J. D. (1976). *Phys. Rev. B* **13**, 5188–5192.

Peiris, S. M., Wong, C. P. & Zerilli, F. J. (2004). *J. Chem. Phys.* **120**, 8060–8066.

Pawley, G., Mackenzie, G., Bokhenkov, E., Sheka, E., Dorner, B., Kalus, J., Schmelzer, U. & Natkaniec, I. (1980). *Mol. Phys.* **39**, 251–260.

Peiris, S. M., Wong, C. P. & Zerilli, F. J. (2004). *J. Chem. Phys.* **120**, 8060–8066.

Perdew, J. P., Burke, K. & Ernzerhof, M. (1996). *Phys. Rev. Lett.* **77**, 3865–3868.

Refson, K. & Payne, M. C. (2005). *Z. Kristallogr. Cryst. Mater.* **220**, 567–570.

Rueckhaus, D., Vohra, Y. & Velisavljevic, N. (2012). *J. Chem. Phys.* **137**, 174304.

Sorescu, D. C., Boatz, J. A. & Thompson, D. L. (2001). *Progr. Nat. Sci. Mater. Int.* **11**, 5010–5021.

Strach, D. & Dorner, B. (1986). *J. Phys. C Solid State Phys.* **19**, 2853–2864.

Su, Y., Fan, J., Zheng, Z. & Zhao, J. (2019). *Progr. Nat. Sci. Mater. Int.* **29**, 329–334.

Tkatchenko, A. & Scheffler, M. (2009). *Phys. Rev. Lett.* **102**, 073005.

Tokmakoff, A., Fayer, M. D. & Dlott, D. D. (1993). *J. Phys. Chem.* **97**, 1901–1913.

Trzcinski, W. & Belaada, A. (2016). *Cent. Eur. J. Energ. Mater.* **13**, 527–544.

Zerilli, F. J. & Kukljica, M. M. (2007). *J. Phys. Chem. A* **111**, 1721–1725.

Zhang, J., Velisavljevic, N., Zhu, J. & Wang, L. (2016). *J. Phys. Condens. Matter.* **28**, 395402.