

# Low-energy phonons in single crystal $\text{ZrW}_2\text{O}_8$

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(Received 14 August 2024; revised 25 February 2025; accepted 16 June 2025; published 7 July 2025)

$\text{ZrW}_2\text{O}_8$  is the prototypical example of a material exhibiting negative thermal expansion (NTE). It is now widely accepted that in  $\text{ZrW}_2\text{O}_8$ , and in many other framework materials exhibiting NTE, a collection of low energy phonon modes, as opposed to just one or two, are responsible for the anomalous thermal properties. However, quantitative verification and analysis of the density functional theory (DFT) calculations which underpin this proposal are still lacking. In particular, probing the low energy phonons directly throughout reciprocal space using inelastic neutron scattering, as opposed to other techniques which only probe the Brillouin zone center, is technically challenging and hence rarely done. Here we report inelastic neutron scattering measurements in a large number of Brillouin zones over a 400 K temperature range. We find excellent agreement between DFT calculations and experimental data at low temperature. However, the shifts in phonon modes predicted by DFT due to the reduction in lattice parameter (warming) are not observed. This is most likely due to counteractive anharmonic effects, which we verified using finite temperature molecular dynamics (MD) calculations. Notwithstanding, both DFT and MD results are consistent with NTE in  $\text{ZrW}_2\text{O}_8$  arising from the tension effect, and by extension this explanation is supported by the neutron scattering results.

DOI: [10.1103/t84f-kg8t](https://doi.org/10.1103/t84f-kg8t)

## I. INTRODUCTION

Negative thermal expansion (NTE) is when a material contracts rather than expands on warming. This effect can be uniform, i.e., along all crystallographic axes [1–3], or nonuniform [4–6]. It may also exist over a wide or a more limited range of temperatures [7].  $\text{ZrW}_2\text{O}_8$  is in many respects the canonical example, with its NTE having been rediscovered in the 1990s [8–10]. It is particularly notable that its NTE behavior is uniform, extant over a wide temperature range, from  $\sim 10$  K to  $\sim 1000$  K, and its coefficient of thermal expansion is large and negative ( $\sim 10^{-5}\text{K}^{-1}$ ) (see review articles Ref. [11] and Ref. [12] and references therein). In common with many other materials known to exhibit NTE,  $\text{ZrW}_2\text{O}_8$  has a framework structure, i.e., it contains many ions that form coordinated polyhedra, most of which share corners, with large pores or spaces between the polyhedra (see Fig. 1). It has also been found that intercalation of water into these pores can also result in significant anomalous lattice expansion or contraction [14].

As a material is warmed, phonon modes with gradually increasing energy are populated. If the potentials for these

modes are asymmetric as a function of displacement, then thermal expansion will arise [15,16]. Studies of the phonons in NTE materials often involve measurement of the phonon density of states (PDOS) using either Raman spectroscopy, inelastic x-ray scattering, or inelastic neutron scattering measurements of powder samples [17–23], as this is relatively straightforward to do and can be compared directly to quasi-harmonic lattice dynamics calculations such as those from density functional theory (DFT).  $\text{ZrW}_2\text{O}_8$  is no exception, with the phonon density of states having been measured as a function of temperature soon after the seminal works on the NTE behavior [24]. It was found that the low energy peaks in the PDOS shift to higher energy on warming. Qualitatively, this is the opposite behavior to normal (positive thermal expansion) in which increased bond lengths on warming typically result in weaker interatomic potentials and hence a reduction in the energy of phonon modes.

In terms of interpretation of the PDOS measurements, and NTE more generally, early theories concerned the role of rigid unit modes (RUMs), in which Zr–O and W–O polyhedra remain undistorted but the whole structure flexes considerably along their shared vertices. As the amplitude of such modes increases, the root-mean-square distance between metal centers decreases, even though individual metal–oxygen bonds do not change in length [11]. Such modes would typically be found at the lower energy end of the phonon spectrum. However, various measurements have indicated that the picture may be somewhat more complex than this. In particular, it has been found from EXAFS [25–27] that all of the polyhedra in the structure distort somewhat on warming, although the  $\text{WO}_4$

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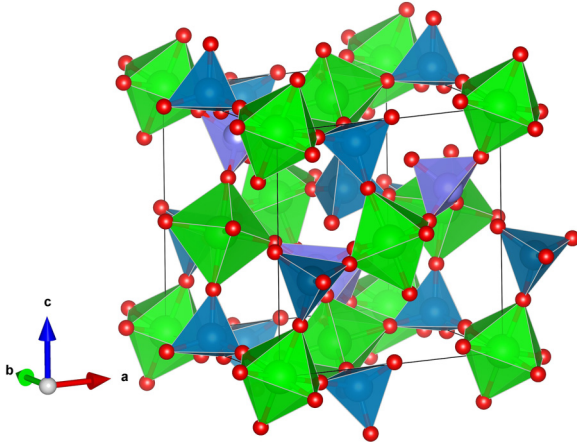


FIG. 1. The crystal structure of  $\text{ZrW}_2\text{O}_8$  (space group  $P2_13$ ) with  $\text{ZrO}_6$  octahedra shaded green and  $\text{WO}_4$  tetrahedra shaded purple and blue, corresponding to tetrahedra centered on the crystallographically distinct W1 and W2 sites, respectively. Note that each  $\text{WO}_4$  tetrahedron contains one unbonded oxygen ion on its vertex, pointing along a local  $\langle 1\ 1\ 1 \rangle$ -direction. This figure was created using VESTA [13].

tetrahedra are noticeably more rigid than the  $\text{ZrO}_6$  octahedra. Notwithstanding, significant flex occurs along some of the  $\text{Zr-O-W}$  bonds that comprise the corner-sharing polyhedra. In this context, it would be appealing to search for a particular phonon mode that facilitates this distortion. However, numerous computational studies of the lattice dynamics in  $\text{ZrW}_2\text{O}_8$  [28–31] have demonstrated that there is no such single mode responsible for NTE. Rather, a large number of low energy phonon modes distributed throughout the Brillouin zone have a character that leads to NTE.

The direct measurements of phonons in  $\text{ZrW}_2\text{O}_8$  (and many other NTE materials) to date have had a number of limitations. Raman spectroscopy can only measure the

Brillouin zone center ( $\mathbf{q} = 0$ ) Raman-active modes and thus does not provide a comprehensive picture, although the energy resolution available with this technique is usually superior to that available with neutron or x-ray spectroscopy. Neutron (or x-ray) scattering PDOS measurements are by their very nature a spherical average over reciprocal space of all possible phonon modes at a particular energy, so there is no direct sensitivity to the  $\mathbf{Q}$ -space origin of shifts in energy with temperature. This can be ameliorated somewhat by interpreting these measurements with DFT calculations. However, this approach is challenging in systems containing many atoms, and hence many phonon modes which may be more closely spaced than the energy resolution of the neutron spectrometer used for the measurements. In contrast, a measurement of a single crystal sample would allow individual modes to be isolated via measurements performed in many different Brillouin zones [32]. This would then provide a more stringent test of the DFT.

The motivation of the present study is therefore to develop a more comprehensive understanding of the low energy phonons in  $\text{ZrW}_2\text{O}_8$ , by measuring in more Brillouin zones using inelastic neutron scattering with good energy resolution, to identify if any particular individual or groups of phonon modes are especially sensitive to temperature. Such measurements are sensitive to both the eigenvalues and eigenvectors extracted from *ab-initio* calculations, and hence pose a stringent test of the range of their validity, most notably for the low energy phonons thought to be important for NTE.

## II. METHODS

Time of flight neutron scattering experiments were performed on the IN5 spectrometer at the Institut Laue-Langevin [33]. Data were collected with incident neutron energies  $E_i = 8.24$  meV and  $E_i = 10.43$  meV, at temperatures in the range 2 K to 400 K. Density Functional Theory (DFT) calculations were performed using the plane-wave pseudopotential method as implemented in the CASTEP package [34]. Calculations

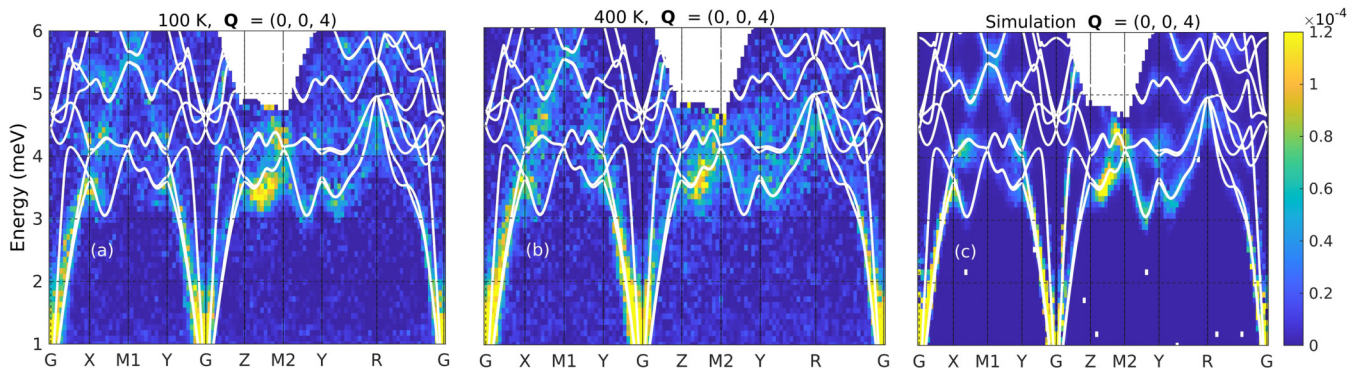


FIG. 2. Slices through the  $\mathbf{Q}$ -Energy plane, following a defined path through along high-symmetry reciprocal space directions. The labeling convention for these high-symmetry positions is  $\Gamma \equiv (0, 0, 0)$ ,  $X = (\frac{1}{2}, 0, 0)$ ,  $M1 = (\frac{1}{2}, \frac{1}{2}, 0)$ ,  $Y = (0, \frac{1}{2}, 0)$ ,  $M2 = (0, \frac{1}{2}, \frac{1}{2})$ ,  $Z = (0, 0, \frac{1}{2})$ , and  $R = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The data and simulations shown in this figure were centered on the  $\mathbf{Q} = (0, 0, 4)$  Brillouin zone. The neutron scattering structure factor (intensity) is indicated by the false colormap. Panel (a) shows data collected at 100 K, panel (b) shows data collected at 400 K, and panel (c) shows simulations of the neutron cross section computed from the DFT calculations with a lattice parameter of 9.215 Å. The data in panels (a) and (b) have had a constant background subtracted and have then been corrected for the Bose-Einstein population factor so that their color scales (which are in arbitrary but consistent units) can be compared directly. The color scale for the simulation in panel (c) is scaled so that the 5% most intense data points match their equivalents in panel (a). The white lines in all three figures correspond to the dispersion relation calculated using DFT with a lattice parameter of 9.215 Å.

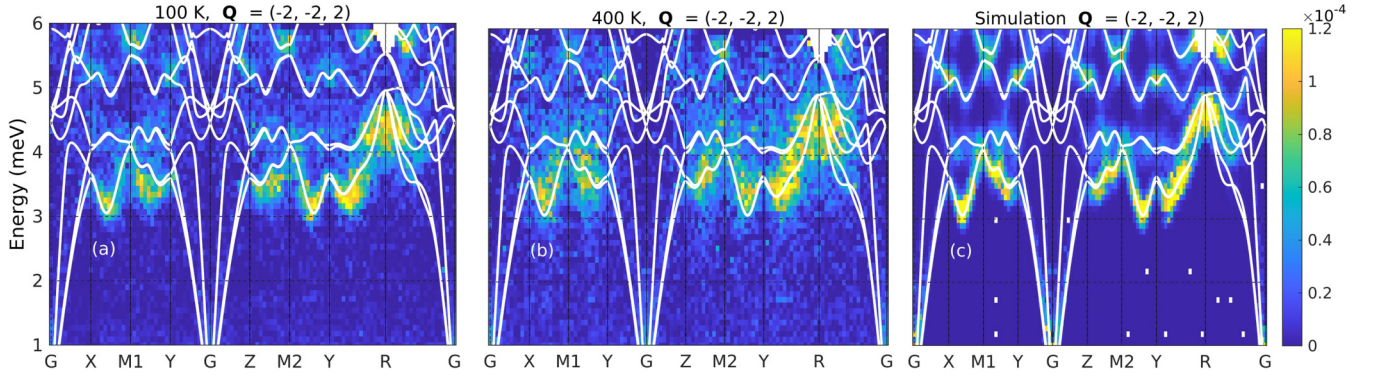


FIG. 3. Slices through the  $\mathbf{Q}$ -Energy plane, following the same scheme as Fig. 2. The data here were centered on the  $\mathbf{Q} = (-2, -2, 2)$  Brillouin zone. Notice that the change in direction of  $\mathbf{Q}$  results in the highest intensity being peaked at different high symmetry positions than for the data shown in Fig. 2.

were performed for a series of different fixed lattice parameters close to the ground state parameters determined from a minimization of the overall forces and energies. Phonon dispersions were calculated using Density Functional Perturbation Theory (DFPT). It is important to note that in DFT the lattice dynamics are calculated at zero temperature in the quasiharmonic approximation. When comparing the computed dispersion with that measured experimentally with neutrons, an empirical scale factor was applied to the eigenvalues (phonon energies) but not to the eigenvectors (structure factors).

Calculations of the finite-temperature behavior of the phonon dispersion at a few high-symmetry wave vectors were performed using machine learned potentials and molecular dynamics (MD). The potentials were computed using the automated potential development (APD) workflow [35]. These potentials were then used for MD simulations, using the LAMMPS software package [36].

Further details of the inelastic neutron scattering experimental methods can be found in the Supplemental Material [32] (see also Refs. [37–58] therein), as can the detailed schemes used for the density functional theory and molecular dynamics calculations.

### III. RESULTS

#### A. INS data

Figure 2 shows slices through the four-dimensional datasets recording  $S(\mathbf{Q}, \omega)$ , in the  $\mathbf{Q}$ -Energy plane [59], following a path through reciprocal space traversing a set of high-symmetry points. Note that although the points labeled as X, Y, and Z; and as M1, M2, and M3 are equivalent by symmetry, there are paths between them that are inequivalent by symmetry because the space group,  $P2_13$ , is noncentrosymmetric. Data are presented centered at  $\mathbf{G} = (0, 0, 4)$  in Fig. 2 and  $\mathbf{G} = (-2, -2, 2)$  in Fig. 3 for both  $T = 100$  K and  $T = 400$  K, and at  $\mathbf{G} = (3, -3, 0)$  in Fig. 4 for  $T = 2$  K and  $T = 300$  K. The DFT-calculated dispersion relation with  $a = 9.215$  Å, with the energy scale reduced by 5%, is overplotted. The calculated structure factor is also shown in panel (c) of all three figures. This set of figures illustrate many of the salient points of this work. It is clear that the dispersion and cross section calculated using DFT provide an extremely good level of agreement with the neutron measurements, with significant overlap at most wave vectors, indicating that both the eigenvalues and eigenvectors from the DFT are accurate.

At most wave vectors a change in temperature of  $\sim 300$  K results in very little change in the measured dispersion and

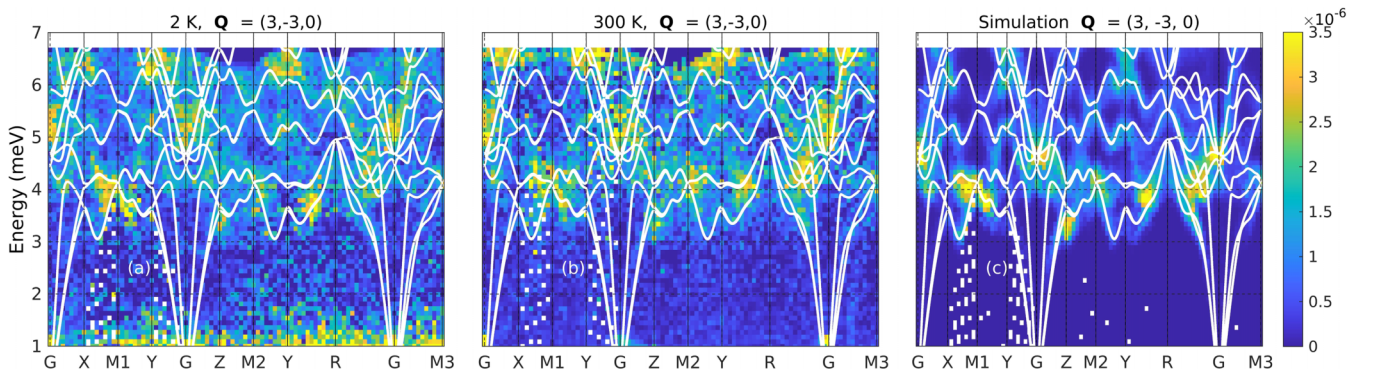


FIG. 4. Slices through the  $\mathbf{Q}$ -Energy plane, following the same scheme as Fig. 2, with the exception of the extra reciprocal lattice point on the right hand side that is labeled M3 and refers to  $(\frac{1}{2}, -\frac{1}{2}, 0)$ . The data here were collected in a separate experiment and are centered on the  $\mathbf{Q} = (3, -3, 0)$  Brillouin zone. Data shown were collected at 2 K and 300 K, which is different to Figs. 2 and 3. The different experiments also have a different (but mutually consistent) set of arbitrary units for the intensity scale. These data are notable by having intensity peaked near the G point, unlike the other two datasets shown, and extending to slightly higher energy.

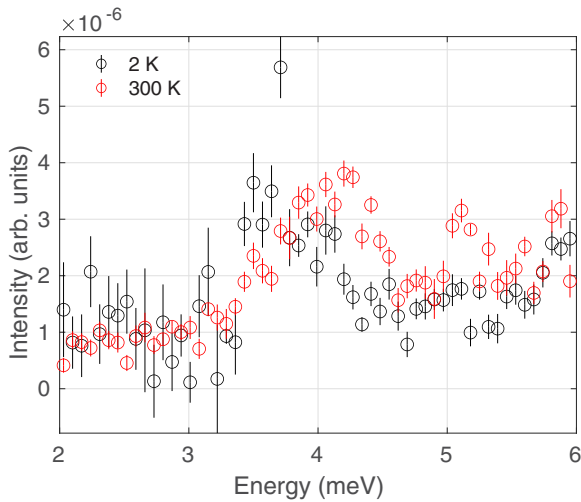


FIG. 5. Cut at the midpoint of the Y-R trajectory of Figs. 4(a) and 4(b), i.e., at  $\mathbf{Q} = (3.25, -2.5, -0.25)$ , showing a hardening of the first phonon peak from  $\sim 3.5$  meV to  $\sim 4$  meV.

$S(\mathbf{Q}, \omega)$ . A broadening of the signal from most of the phonons modes, indicative of anharmonicity at elevated temperatures, is observed. One notable exception is that on warming from 2 K to 300 K a significant mode hardening of around 0.5 meV is seen on the mode between the Y and R points in Fig. 4. To show this in more detail a cut at the midpoint,  $\mathbf{Q} = (3.25, -2.5, -0.25)$ , is shown in Fig. 5. Modes along similar trajectories in the reduced Brillouin zone in the other datasets (Figs. 2 and 3) do not show such a dramatic shift. However, we can see from careful inspection of the DFT-calculated dispersion at the Y point that what appears to be a single mode is actually two different ones with only a small separation in energy. The fact that the two modes appear to behave differently with temperature is a good illustration of the power of measuring in multiple Brillouin zones - with only the data centered on  $(-2, -2, 2)$  and  $(0, 0, 4)$  this effect would not have been visible. A similar, although less dramatic, mode hardening occurs at the midpoint of the Z-M2 trajectory (equivalent by symmetry to Y-M1), which is visible in both Figs. 2 and 3, and is shown as a cut in Fig. 6.

Despite the overall excellent agreement between the DFT calculations and the INS measurements shown in Figs. 2–4, there is some disagreement. An example can be seen by comparing the calculated dispersion and cross section shown in panel (c) with the data in panels (a) and (b) of all three figures. For example, we can see that for the lowest energy mode on the path M1 – Y (and M2 – Z, which is equivalent by symmetry) the calculated energy is rather higher than the measurement at 100 K, whereas the other low energy ( $< 4$  meV) modes along other paths agree rather closely at this temperature.

To allow a more quantitative analysis we show constant  $\mathbf{Q}$  cuts along the energy axis at various high symmetry wave vectors, G, X, M, and R, at different temperatures in Fig. 7. In all cases the integration range along the orthogonal  $q$ -axes is 0.04 reciprocal lattice units. This finite integration range, necessary when plotting data from time-of-flight INS experiments, obviously means that for modes that are highly dispersive near

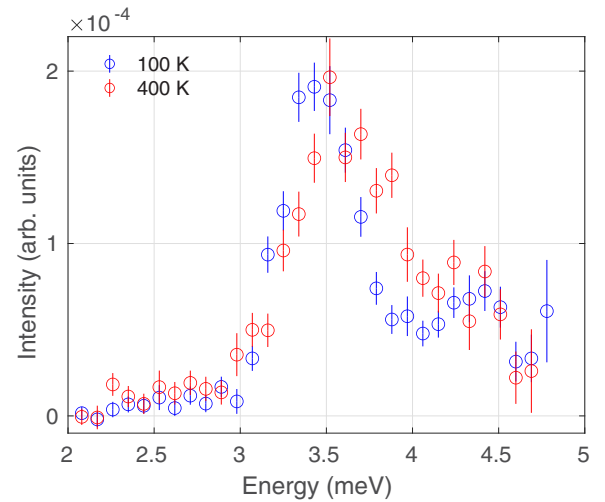


FIG. 6. Cut at the midpoint of the Z-M2 trajectory of Figs. 2(a) and 2(b), i.e., at  $\mathbf{Q} = (0, 0.25, 4.5)$ , showing a slight hardening of the first phonon peak from  $\sim 3.4$  meV to  $\sim 3.5$  meV.

the wave vector of interest the width of peaks may be broader than the nominal instrumental energy resolution. This is most apparent for the single peak in the cut at R—referring to Fig. 3 one can see that the dispersion is very steep until quite close to the R point.

## B. DFT calculations

The DFT calculations plotted in Figs. 2–4 were performed at a lattice parameter of 9.215 Å, and we then reduced all calculated phonon energies by 5% to give best agreement with the INS measurements [60].

We show in Fig. 8 the effect of the lattice parameter on the computed phonon spectra below 6 meV (the energy range covered in our INS experiments). As would be expected from the Grüneisen parameters reported in the literature, the low energy phonons are mostly found to harden with increasing lattice parameter. However, the scaling is not uniform, as can be seen in the inset which shows the trajectory along Z – M2 – Y. For instance, the two lowest energy modes for  $a = 9.210$  Å and  $a = 9.215$  Å are relatively flat in energy, whereas the equivalent modes for  $a = 9.259$  Å are much more dispersive. Furthermore, one can see that at the M2 point the highest energy mode decreases by  $\sim 0.2$  meV on compression of the lattice from  $a = 9.259$  Å to  $a = 9.215$  Å ( $\Delta a = -0.044$  Å) and decreases by even more,  $\sim 0.3$  meV, for further compression  $\Delta a = -0.005$  Å. As noted above, we compared the INS data with the calculations for the unit cell with  $a = 9.215$  Å rather than  $a = 9.259$  Å, which is the zero-stress optimized unit cell dimension in the DFT, or the cell with  $a = 9.210$  Å. Globally rescaling the phonon energies in either of the latter two sets of calculations resulted in worse agreement with the neutron data.

As noted, a small compression of the lattice from  $a = 9.215$  Å to  $a = 9.210$  Å yields a rather large change in mode energies, suggesting that around these lattice parameters the calculations are on the edge of dynamical stability. Indeed, when the lattice was compressed further in the

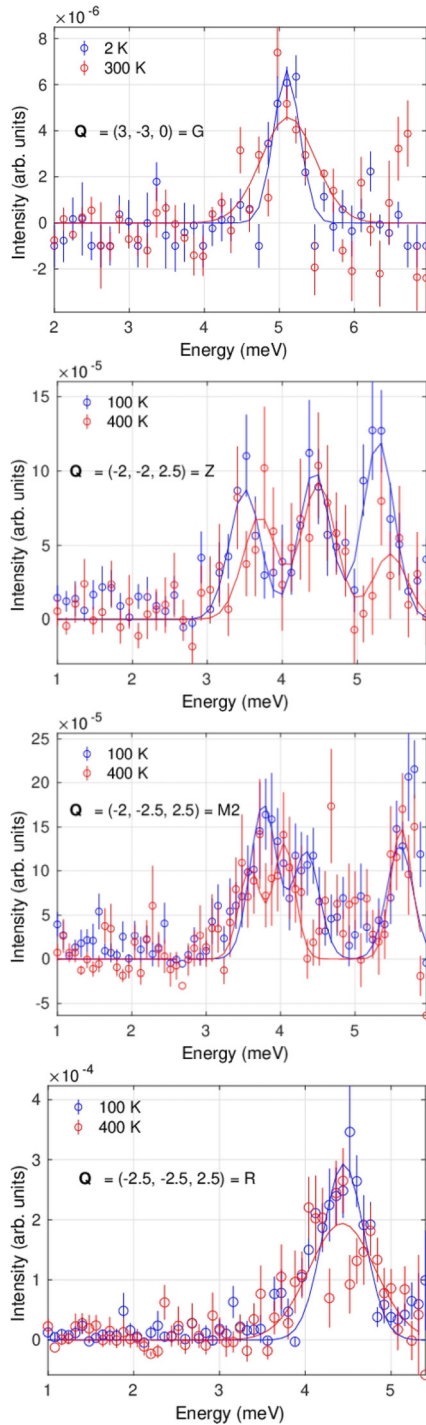


FIG. 7. Cuts along the energy axis at four high symmetry positions in reciprocal space, centered on different Brillouin zones in order to maximize the cross section. Panel (a) shows a cut at G, panel (b) a cut at Z, panel (c) a cut at M2, and panel (d) a cut at R. Data at lower temperatures [2 K in panel (a), 100 K in panels (b)–(d)] are shown in blue whereas data at higher temperatures [300 K in panel (a), 400 K in panels (b)–(d)] are shown in red. For all cuts an estimated constant background has been subtracted, followed by correction for the Bose-Einstein population factor in order to allow easier comparison of data taken at different temperatures. Solid lines correspond to fits to Gaussians (the number of which is set by the number expected from the DFT calculations), to indicate the peak positions.

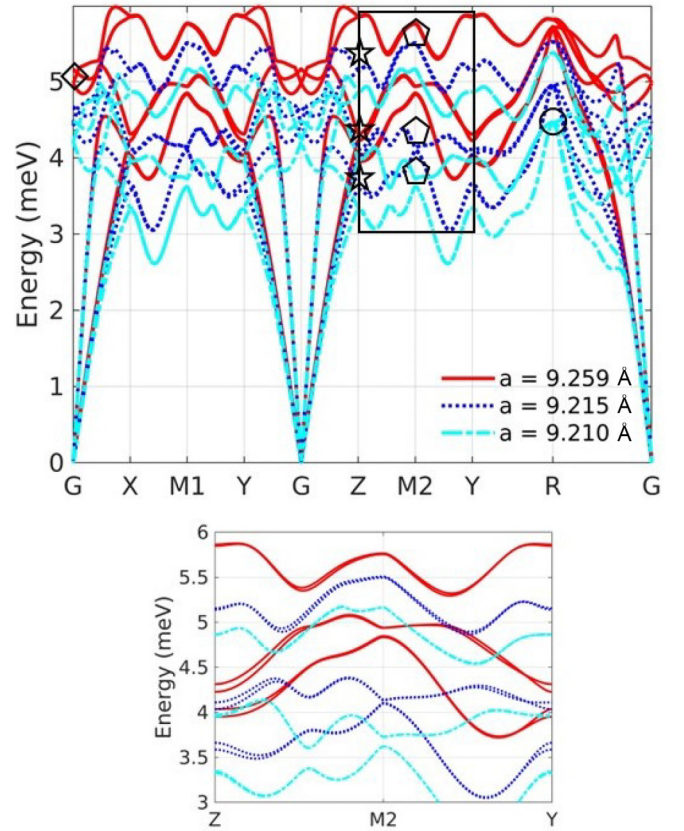


FIG. 8. Comparison of dispersion from DFT calculations with different lattice parameters. The reciprocal space path is the same as described in Fig. 2. The solid red curve is for calculations with lattice parameter  $a = 9.259$  Å (zero stress, optimized lattice parameter), the dotted blue curve is for calculations with  $a = 9.215$  Å, and the dash-dotted cyan curve is for calculations with  $a = 9.210$  Å. The inset shows an enlarged section of the dispersion between 3 and 6 meV. The symbols at high symmetry wave vectors correspond to the fitted peak positions for the lower temperature datasets shown in Fig. 7, with diamonds for the Gamma - point, stars for the Z - point, pentagons for the M2 - point and a circle at the R - point.

DFT calculations (not shown), a significant number of soft modes appeared, consistent with this interpretation. With further compression negative energy modes appear, indicating a change in the ground state structure. Given this nonlinear behavior, to make a quantitative prediction for the effect on the phonon energies of temperature-induced lattice compression in this quasiharmonic approximation, it makes most sense to compare the calculations with  $a = 9.259$  Å and  $a = 9.215$  Å, rather than those with  $a = 9.215$  Å and  $a = 9.210$  Å. The relative difference in the former two lattice parameters is 0.48%, which is quite close to the experimentally observed change in lattice parameter on warming from 100 K to 400 K (0.37%). Thus, one can take the changes in the phonon dispersion between these two calculations as representative of the changes in the phonon dispersion over the experimentally probed temperature range, based on the Grüneisen model alone. The results of this procedure at various high symmetry wave vectors are presented in Table I.

TABLE I. Comparison of the position of the lowest energy peak in the measured data at 100 K and 400 K, and the expected change in peak position based on DFT alone (i.e., quasiharmonic approximation), and the computed change in peak position from the work of Gupta *et al.* [30], decomposed into the contributions from implicit and explicit anharmonicity, from a phenomenological model.

| Wave vector | Lowest energy peak at<br>100 K (meV) | Lowest energy peak at<br>400 K (meV) | DFT shift (meV)<br>[this work] | Calculated shift [implicit<br>+ explicit] (meV) [30] |
|-------------|--------------------------------------|--------------------------------------|--------------------------------|------------------------------------------------------|
| G           | 5.10(3)                              | 5.12(5)                              | −0.55                          | −0.07 [−0.22 + 0.15]                                 |
| Z           | 3.50(5)                              | 3.70(10)                             | −0.40                          | 0.08 [−0.14 + 0.22]                                  |
| M           | 3.77(4)                              | 3.58(7)                              | −0.78                          | 0.06 [−0.36 + 0.42]                                  |
| R           | 4.45(2)                              | 4.43(5)                              | −0.80                          | −0.77 [−0.39 − 0.38]                                 |

The DFT calculations presented so far correspond to the lattice contracting or expanding under pressure/stress, rather than warming/cooling. In reality, the warming will result in an increased amplitude of atomic vibrations, which is not accounted for in the quasiharmonic approximation. Anharmonic effects may become more significant at higher temperatures. This point has been discussed extensively by Mittal *et al.* [12,30], who have calculated these effects for a few individual modes at particular wave vectors in  $\text{ZrW}_2\text{O}_8$ . Some attempt has been made to quantify the effect more broadly using Raman spectroscopy data [17,18], which has indicated that as well as having large negative Grüneisen parameters, the lowest energy modes also have the largest anharmonicity.

The effects of temperature on phonons can be decomposed into two parts. On the one hand a change in lattice parameter with temperature often gives rise to a changed bond length between atoms hence a change in phonon energy. This is sometimes referred to as implicit anharmonicity. In conventional materials, increased temperature gives longer and weaker bonds, and hence softened phonons. On the other hand, as temperature increases phonon-phonon interactions become increasingly important, sometimes also referred to as explicit anharmonicity, and renormalize the phonon energies. This often yields phonon modes that harden slightly with increasing temperature [16]. However, in practice in conventional materials this effect is often much smaller than the softening due to thermal expansion and so is masked.

In Table I we compare the positions of peaks in the INS signal at high symmetry wave vectors as a function of temperature, with the expected shift due to a change in lattice parameter alone from the DFT. Additionally, we compare these results to phenomenological calculations by Gupta *et al.* [30] that decompose the shift into components arising from implicit and explicit anharmonicity. With the exception of the calculation at the R-point, the changes in peak position from the latter are much smaller than those predicted from the DFT alone, and are closer in magnitude to the effects seen in the INS measurements.

### C. Machine learned potentials and molecular dynamics calculations

An alternative way of analyzing the phonons, that explicitly includes finite temperature effects, is to use molecular dynamics (MD) calculations. The approach we took was to use the APD framework for machine-learned interatomic potentials [35], an approach for  $\text{ZrW}_2\text{O}_8$  closely related to that used in Ref. [61]. A detailed technical description of the

methodology is provided in the Supplemental Material [32]. The resulting interatomic potentials can be used to interrogate material properties at finite temperatures. For convenience, we used the PBEsol functional for the underpinning DFT that was used to generate the training data for the potentials. The potentials from this were optimized after four active learning cycles. As a check on results, the temperature-dependent lattice parameter was computed. A coefficient of linear thermal expansion of  $-6.04 \times 10^{-6} \text{ K}^{-1}$  was found. This is a slight underestimate compared to the experimental value of  $-9.37 \times 10^{-6} \text{ K}^{-1}$ , but it is crucially the correct sign and is similar in magnitude to that found by He *et al.* [61]. The phonon dispersion obtained from the trained potentials was also verified against the zero temperature DFT dispersions.

In order to compare the MD results to the INS data, dynamical structure factor calculations were performed with the lattice parameters fixed to the time-averaged values at each temperature. Gaussians were then fitted to the peaks in energy scans up to 6 meV at several high symmetry wave vectors to quantify the temperature-dependent shifts in these modes. The results are shown in Fig. 9, with the energy scans shown in the Supplemental Material [32]. The majority of the modes harden slightly on warming, with the exception of the highest energy one at the M point [ $\mathbf{q} = (0.5, 0.5, 0)$ ] which softens slightly. We note that between 100 K and 400 K the calculated

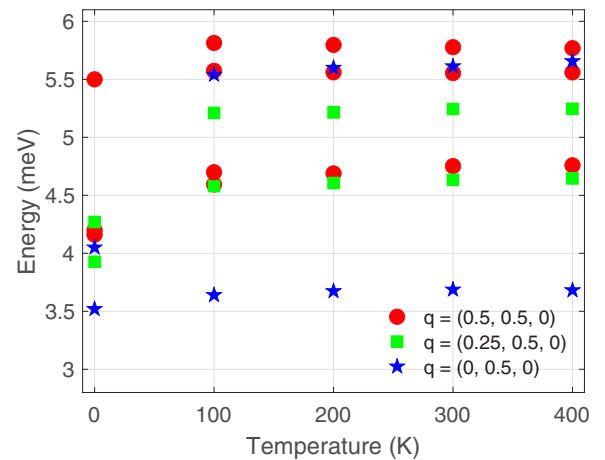


FIG. 9. Temperature dependence of phonon modes below 6 meV computed using MD with machine-learned potentials. Red circles indicate the modes at  $\mathbf{q} = (0.5, 0.5, 0)$  (M1 in the notation of Fig. 2), green squares the modes at  $\mathbf{q} = (0.25, 0.5, 0)$ , and blue circles the modes at  $\mathbf{q} = (0, 0.5, 0)$  (Y in the notation of Fig. 2).

magnitude of mode hardening of  $\sim 0.1$  meV is similar in magnitude to what is seen in our INS measurements. But between 0 K and 100 K a much greater mode hardening is predicted, notably with the modes at  $\mathbf{q} = (0, 0.5, 0)$  and  $\mathbf{q} = (0.25, 0.5, 0)$  hardening on warming by  $> 0.5$  meV, which is not observed in the measurements. This may, for example, be due to the precise choice of functional used for the DFT training data on which the interatomic potentials were based. We note that the DFT calculations presented in Sec. III B had to be fine-tuned for best agreement with the data, whereas the DFT training data for the MD calculations were not adjusted in this way.

#### IV. DISCUSSION AND CONCLUSIONS

From the results and analysis presented, we can see that there is very good agreement between the phonon dispersion relations and structure factors measured in our inelastic neutron scattering experiments, and those computed from DFT in the zero-temperature quasiharmonic approximation, albeit with a compressed lattice compared to the optimized value. The agreement is good throughout reciprocal space, which is important in the context of the view that there is no single phonon mode responsible for NTE in  $\text{ZrW}_2\text{O}_8$ , but many. This therefore supports the usefulness of the DFT results in interpreting the physics of NTE in  $\text{ZrW}_2\text{O}_8$ . We do not observe any significant change in the neutron structure factors as a function of temperature, aside from some modes broadening on warming, so we can be confident that the phonon eigenvectors do not change significantly with temperature. The fundamental nature of the atomic motions thus do not change with temperature, which is consistent with DFT.

On the other hand, the DFT predicts softening of most phonon modes on compression of the lattice, and with NTE such a compression happens on warming. But we observe that the majority of phonons do not soften, indeed some harden by an amount ( $\sim 0.1$  meV) that is just discernible with our instrumental resolution. This is because DFT's quasiharmonic calculations only capture the lattice compression on warming, but do not capture the full anharmonicity, which plays an increasing role with increasing temperature. Finite temperature effects can be included in MD simulations, which in our case used potentials generated through machine learning applied to DFT. Our MD simulations showed that the low

energy modes at a few high-symmetry wave vectors do indeed harden slightly on warming. A larger hardening than what is observed was predicted between 0 K and 100 K, but as already noted this may be due to the specific choice of functional for the DFT training data for the generation of the interatomic potentials.

Given that the DFT calculations give good phonon eigenvectors when compared to experiment, and the MD calculations show the right behavior of the phonon eigenvalues as a function of temperature when compared to experiment, it is instructive to examine the underlying atomic motions that are common to both to help us understand NTE in  $\text{ZrW}_2\text{O}_8$ . Such analysis has been done separately for the DFT [28] and MD [61], respectively. The former analysis compares the DFT to a set of simplified flexibility models, and concludes that NTE arises due to a tension effect involving nearly rigid Zr–O and W–O bonds, with low energy phonons likely involving quasi-rigid small whole-body rotations of the  $\text{WO}_4$  tetrahedra. The analysis of the MD shows that with increasing temperature the Zr–O and W–O bond lengths indeed change very little, with a small positive expansion, but the W–O–Zr bond angle changes significantly, that could also be described as a tension effect. Our INS data are consistent with both sets of analysis, and both point towards the same basic mechanism of NTE.

#### ACKNOWLEDGMENTS

We are grateful to D. Voneshen (ISIS) and R. Fair (STFC-SCD) for their advice and assistance on the use of Euphonic. We are indebted to M. Dove (QMUL) for his insightful and informative comments. We thank the Institut Laue-Langevin for the allocation of beamtime for the experiments reported here. Computing resources were provided by the STFC Scientific Computing Department's SCARF cluster. A.I.D. gratefully acknowledges funding from the Ada Lovelace Centre (ALC) at the Science and Technology Facilities Council (STFC) and from the Research Council of Norway under Project "Neutron Scattering and Atomistic Simulations for a SUPERior Understanding of SUPERionic Conduction" (Project No. 344062).

#### DATA AVAILABILITY

Raw data are available via Ref. [62] and processed data via Ref. [63].

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