1 Sample Preparation

Na_3PS_4 is prepared by heating a stoichiometric amount of Na_2S and P_2S_5 in an evacuated Pyrex ampule. Na_2S and P_2S_5 were mixed in 3:1 ratio and hand-grounded for 30 minutes in an Argon-filled glovebox with a mortar and pestle. The mixture was evacuated in a Pyrex ampule for 1 hour and sealed with a propane torch. The contents of the ampule were reacted in a box furnace (Nabertherm) by heating the materials to 550 °C at 5 °C/min, held isothermally at 550 °C for 1 hour, cooled to 500 °C at 1 °C/min, held isothermally at 500 °C for 12 hours, and then cooled to room temperature. The materials were collected and hand ground with a mortar and pestle in an Argon-filled glovebox. The formation of a single-phase Na_3PS_4 sample was confirmed from powder XRD (fig S12). All samples were sealed under Kapton film before collecting XRD data.

Table S1 The calculated phonon eigenvectors and NEB derived eigenvectors of the lowest H-point in Na_3PS_4 with Na at $6b$ Wyckoff site (equilibrium) and, $12d$ Wyckoff site (saddle point).

	At equilibrium		At saddle point	
Atom	Phonon Eigenvector ($\zeta^{H}_{\text{phonon}}$) (x,y,z)	NEB Eigenvector (ζ^{6b}_{NEB}) (x,y,z)	Phonon Eigenvector ($\zeta'^{H}_{\text{phonon}}$) (x,y,z)	NEB Eigenvector (ζ^{12d}_{NEB}) (x,y,z)
Na	(0.02, 0.01, 0.00)	(0.00, 0.00,-0.07)	(0.00, 0.00, 0.07)	(0.00, 0.00, 0.02)
Na	(0.02, 0.00, 0.37)	(0.00, 0.00, 0.32)	(0.00, 0.00, -0.14)	(0.00, 0.00,-0.19)
Na	(0.00,-0.01,-0.37)	(0.00, 0.00,-0.49)	(0.00, 0.00,-0.58)	(0.00, 0.00,-0.63)
Na	(0.02,-0.01, 0.00)	(0.00, 0.00,-0.07)	(0.00, 0.00, 0.07)	(0.00, 0.00, 0.02)
Na	(-0.02, 0.00,-0.37)	(0.00, 0.00,-0.49)	(0.00, 0.00,-0.58)	(0.00, 0.00,-0.63)
Na	(0.00, 0.01, 0.37)	(0.00, 0.00, 0.32)	(0.00, 0.00,-0.15)	(0.00, 0.00,-0.19)
P	(0.00, 0.00, 0.00)	(0.00, 0.00,-0.08)	(0.00, 0.00, 0.10)	(0.00, 0.00, 0.04)
P	(0.00, 0.00, 0.00)	(0.00, 0.00,-0.08)	(0.00, 0.00, 0.10)	(0.00, 0.00, 0.04)
S	(-0.17, 0.17, 0.00)	(-0.12, 0.12,-0.09)	(0.10,-0.10, 0.11)	(0.06,-0.06, 0.04)
S	(-0.16, 0.16, 0.00)	(-0.12, 0.12, -0.09)	(0.10, -0.10, 0.11)	(0.06, -0.06, 0.04)
S	(-0.17,-0.16,-0.01)	(-0.12,-0.12,-0.08)	(0.10, 0.10, 0.11)	(0.12, 0.10, 0.05)
S	(0.16, 0.17, 0.01)	(0.12, 0.12,-0.08)	(-0.10,-0.10, 0.11)	(-0.12,-0.10, 0.05)
S	(0.17,-0.17, 0.00)	(0.12,-0.12,-0.09)	(-0.10, 0.10, 0.11)	(-0.06, 0.06, 0.04)
S	(0.16,-0.16, 0.00)	(0.12,-0.12,-0.09)	(-0.10, 0.10, 0.11)	(-0.06, 0.06, 0.04)
S	(0.17, 0.16, 0.01)	(0.12, 0.12,-0.08)	(-0.10, 0.10, 0.11)	(-0.10,-0.12, 0.05)
S	(-0.16,-0.17,-0.01)	(-0.12,-0.12,-0.08)	(0.10, 0.10, 0.11)	(0.10, 0.12, 0.05)

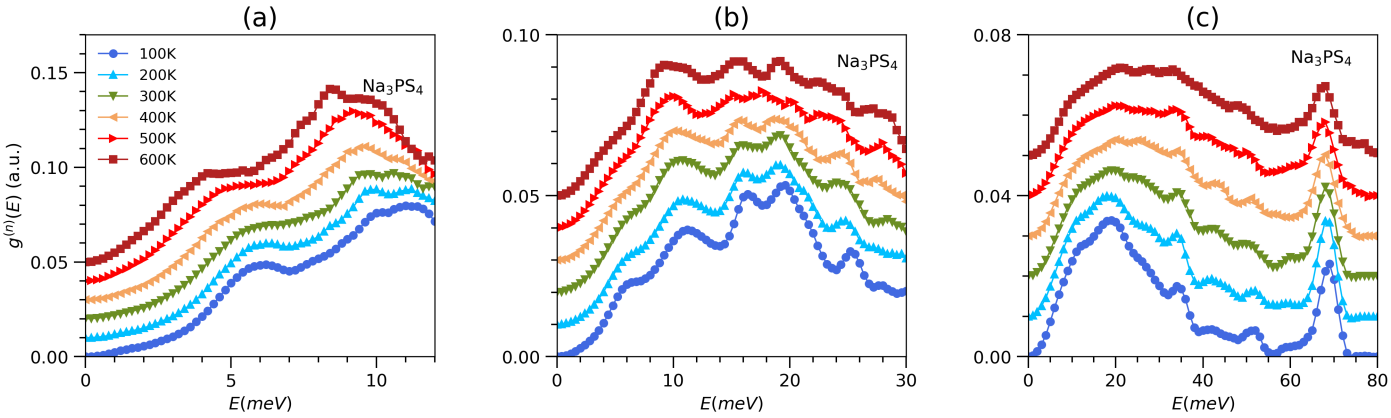

Figure S1 Temperature dependence of INS spectra of Na_3PS_4 measured at ARCS with different incident neutron energy of (a) 20 meV, (b) 40meV, and (c) 100 meV.

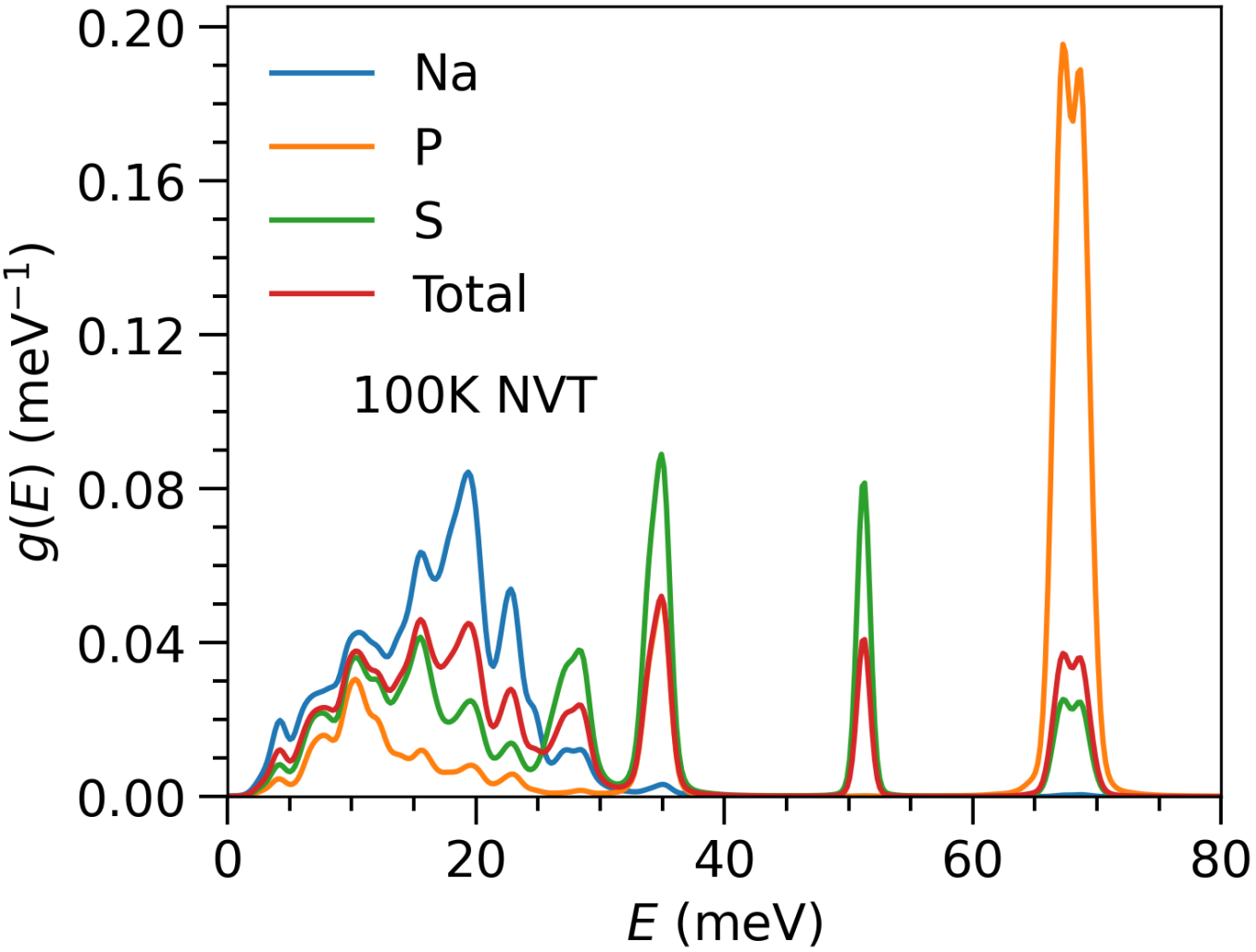

Figure S2 (a-b) The calculated species resolved and total phonon DOS of Na_3PS_4 at 100 K using NVT MLMD. Each plot is normalized to unity.

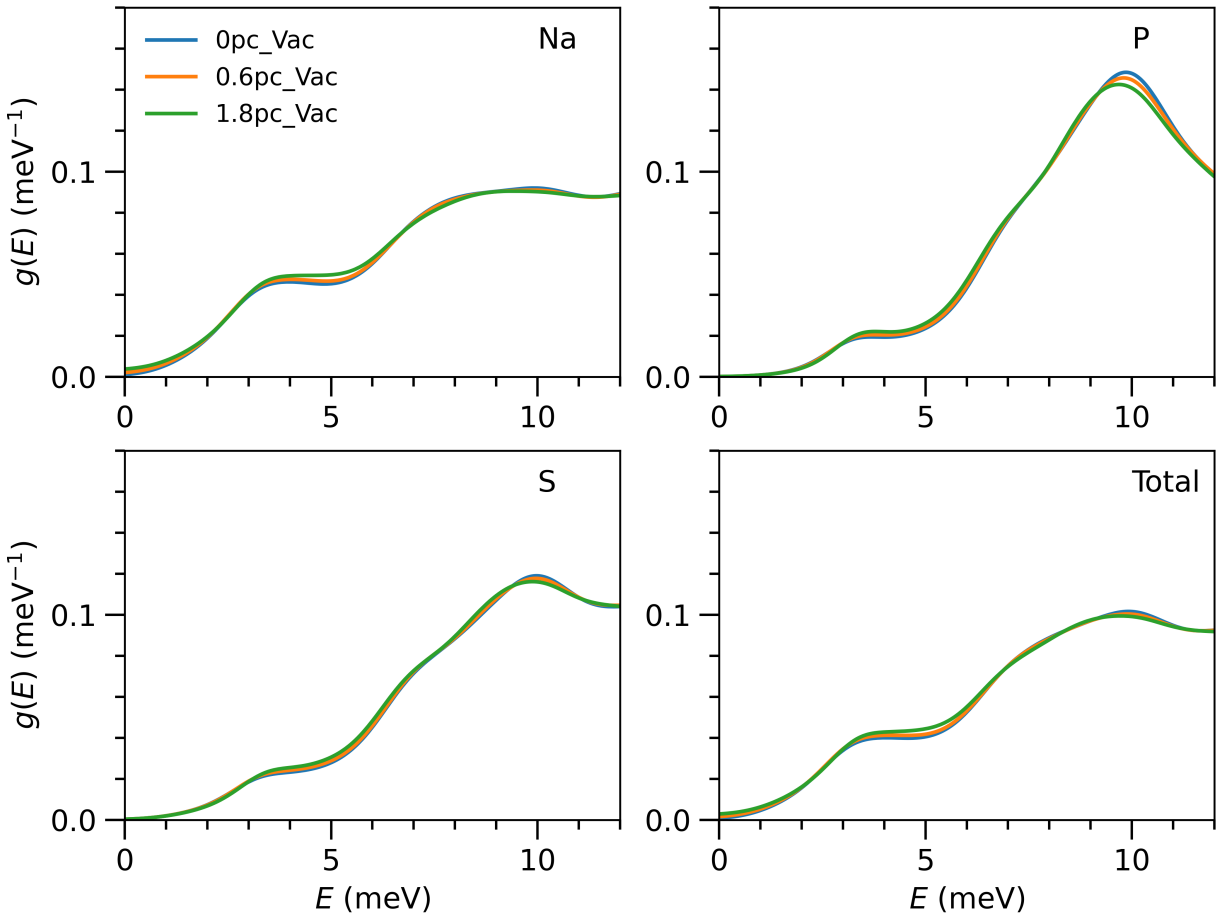

Figure S3 The calculated total phonon DOS with different % Na vacancies in Na_3PS_4at 600 K. For better visibility, we have shown only up to 12 meV.

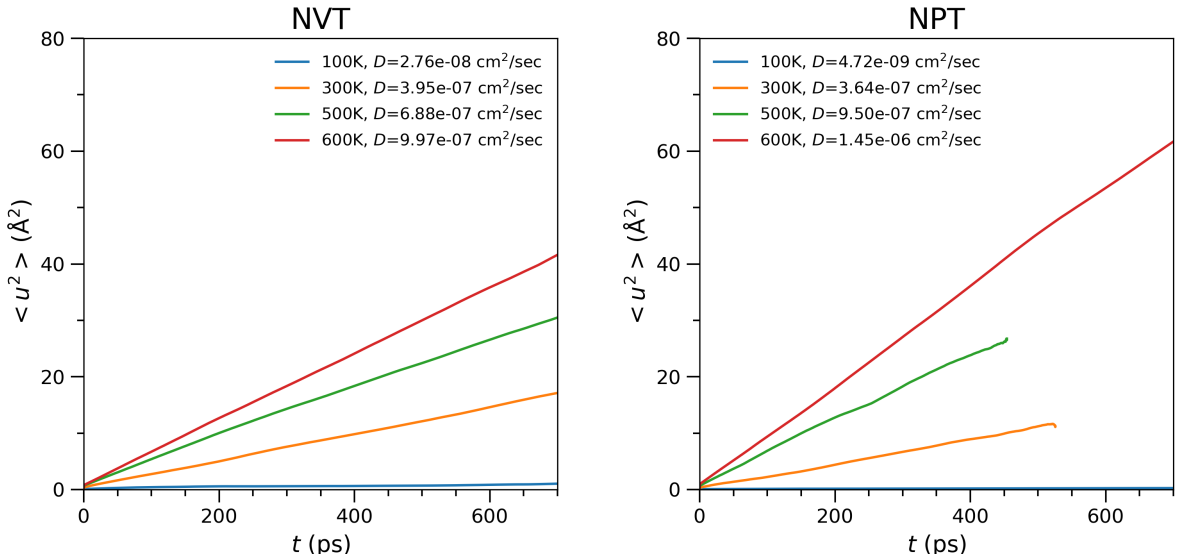

Figure S4 The calculated $< u^2 >$ of Na in Na_3PS_4 with 0.6% Na vacancy from NPT and NVT simulation.

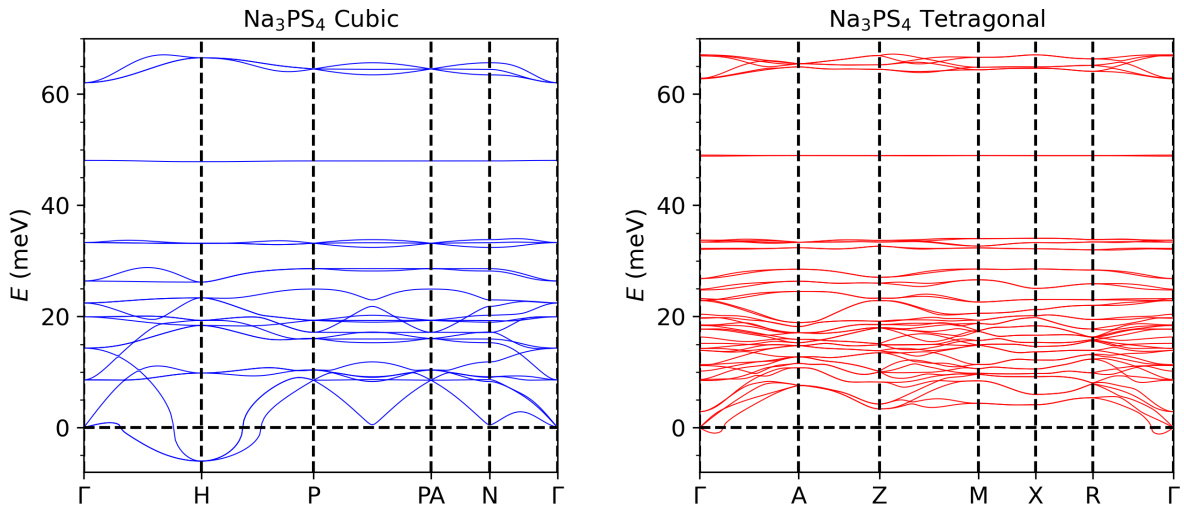

Figure S5 (a-b) The calculated phonon dispersion relation in tetragonal and cubic phases of Na_3PS_4 at T= 0 K within quasi-harmonic approximation.

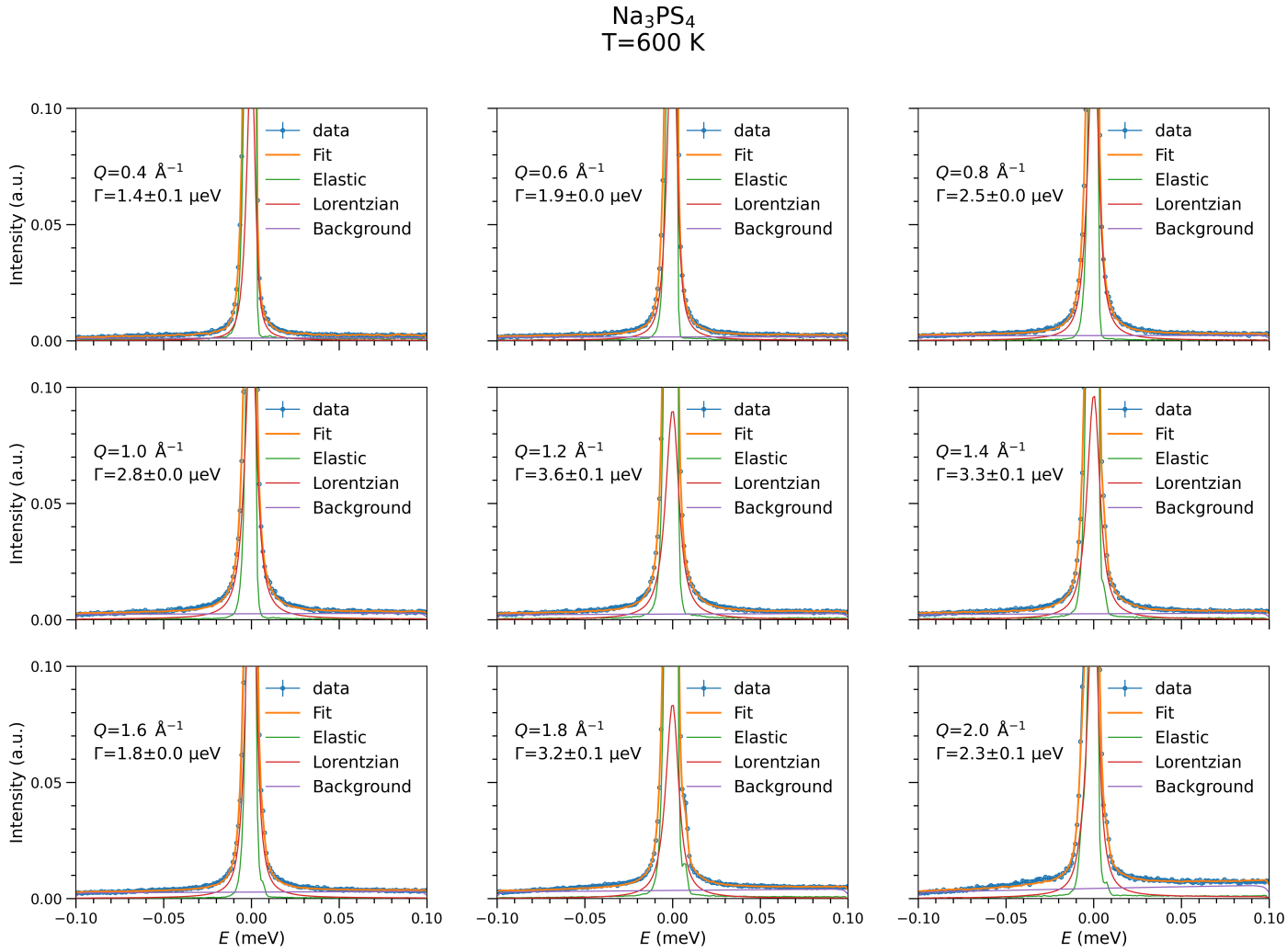

Figure S6 The measured QENS spectra (blue markers) of Na_3PS_4 as a function of Q at 600 K. The measured spectra is fitted with a Lorentzian and delta-function convoluted with resolution function (100 K data) and linear background. Total fit is shown by orange line. The elastic, quasi-elastic and background component of fit is shown by green, red and purple lines, respectively.

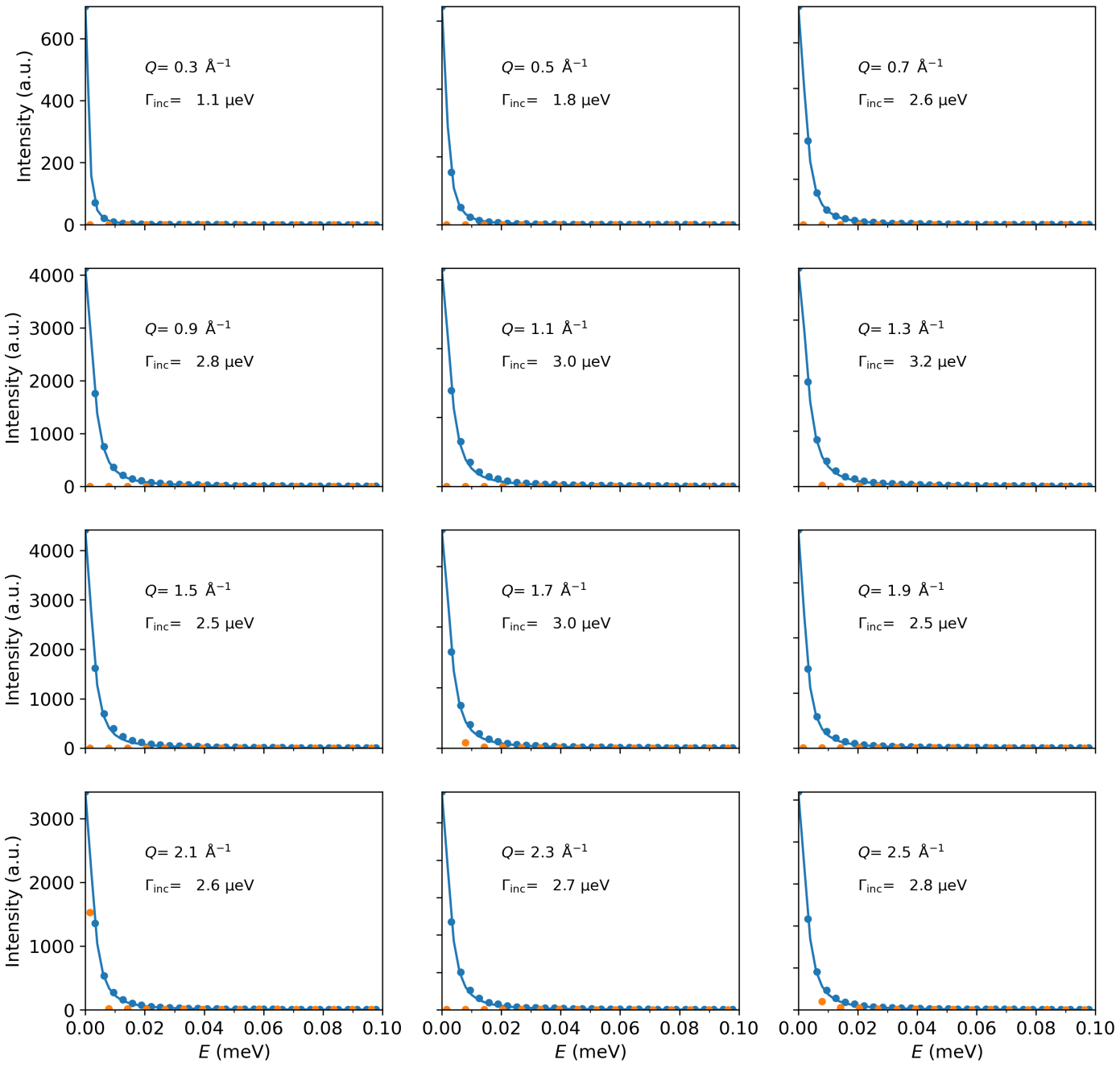

Figure S7 The simulated $S_{coh}(Q,E)$ (orange dots) and $\mathrm{S_{incoh}(Q,E)}$ (blue dots) of Na_3PS_4 with 0.6% Na vacancy 600 K. This infers the QENS spectra has dominant contribution from $\mathrm{S_{incoh}(Q,E)}$ (random diffusion)

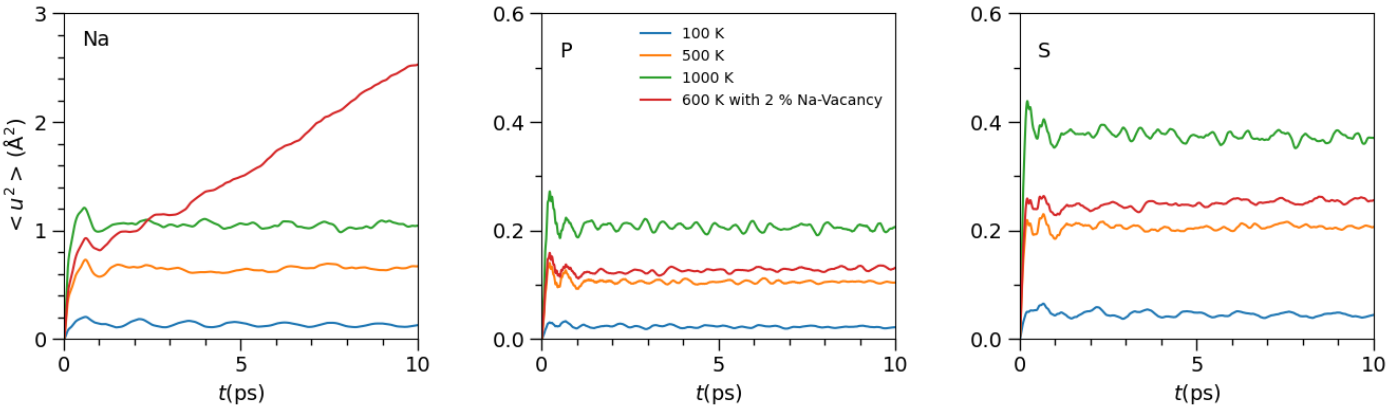

Figure S8 The calculated $< u^2 >$ of each element in stoichiometric and 2% Na vacancy Na_3PS_4 from AIMD simulations. Stoichiometric Na_3PS_4 does not show Na diffusion even up to 1000/,K, and only exhibits Na diffusion in presence of Na vacancy.

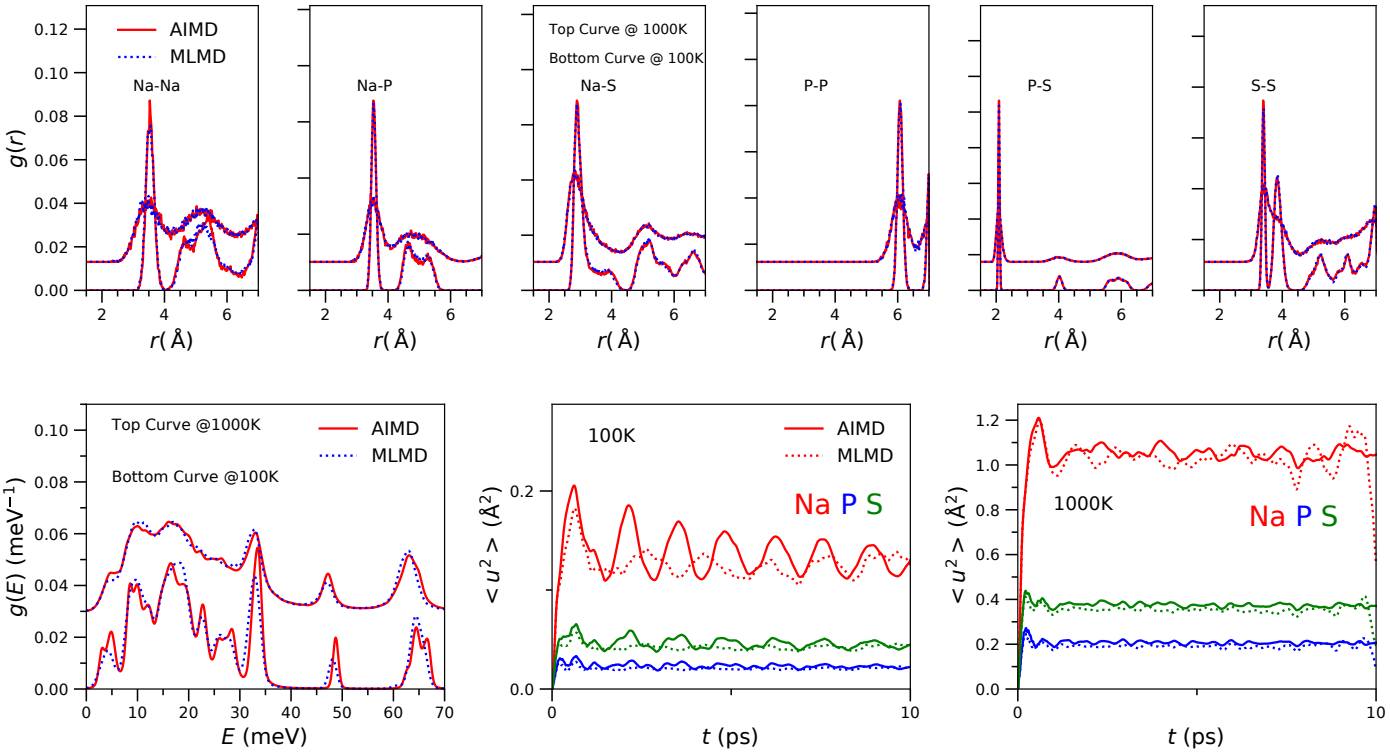

Figure S9 Validation of MLMD force-field (dashed blue line) against AIMD simulation(solid red line) by comparing the (a) pair distribution function (g(r)) between various pairs of atoms in Na_3PS_4, (b) total phonon DOS and (c) $< u^2 >$ of each element in Na_3PS_4 at 100 K and 1000 K.

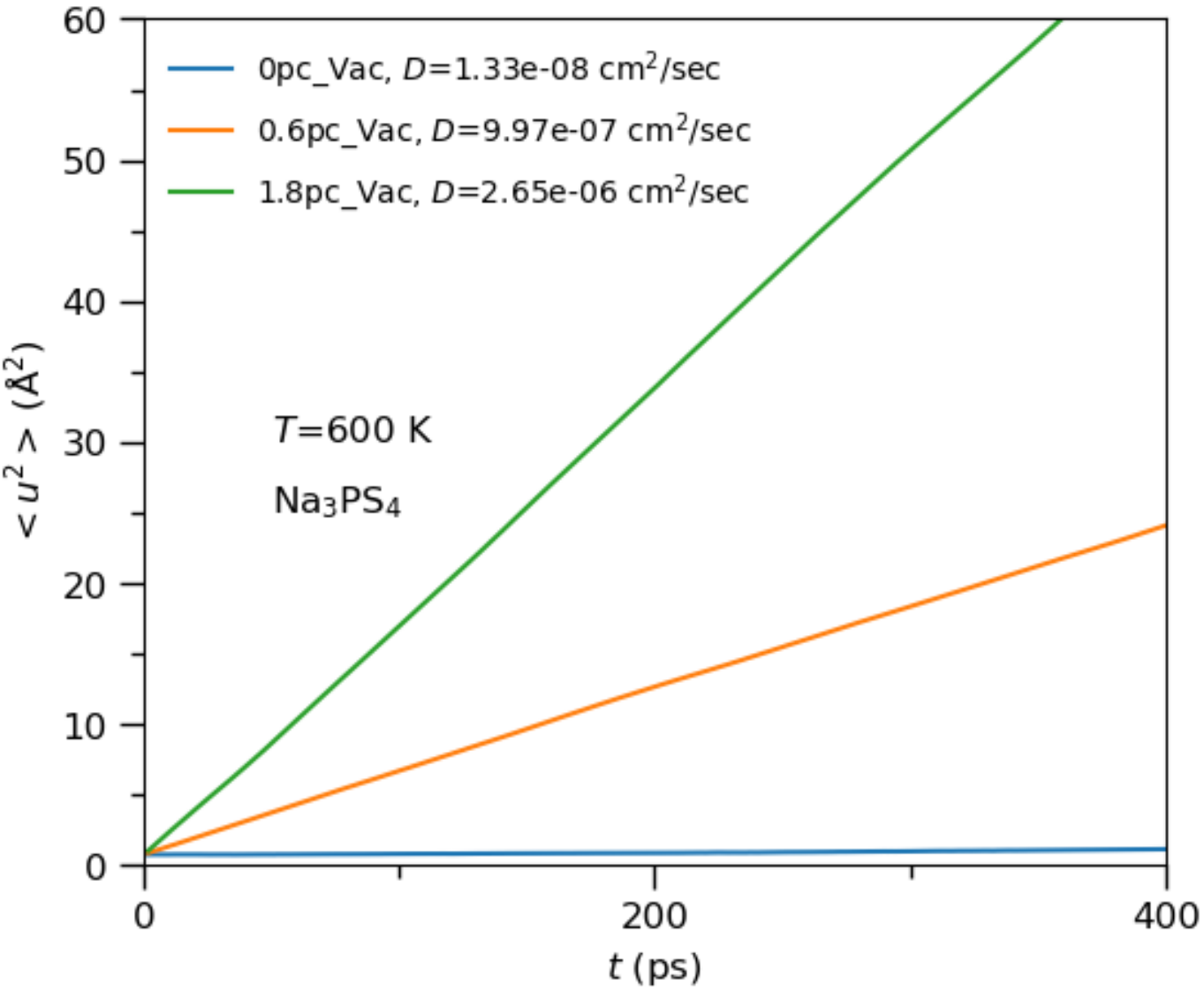

Figure S10 The NVT-MLMD calculated $\langle u^2 \rangle$ of Na in presence of different concentration of Na vacancies in Na_3PS_4.

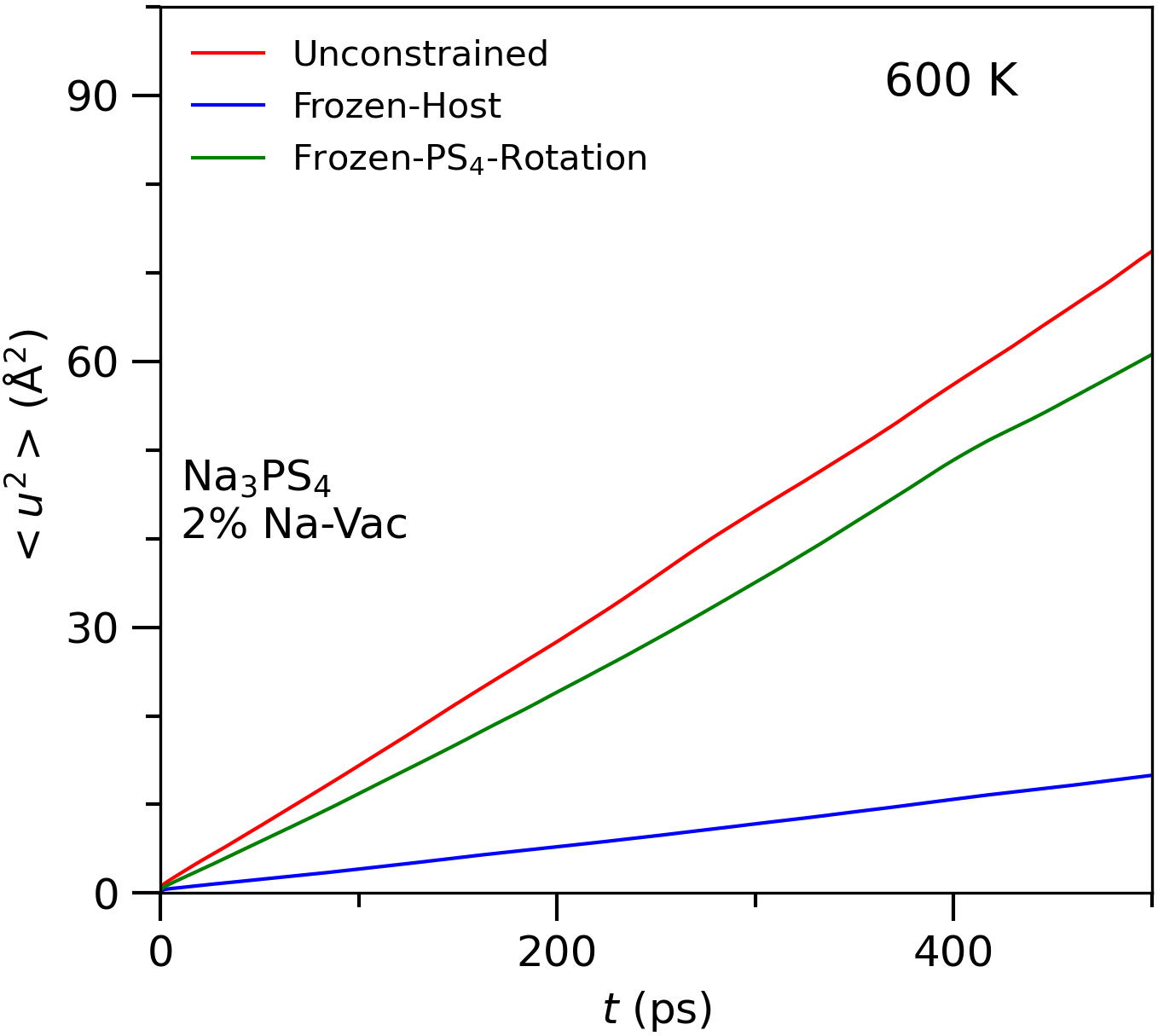

Figure S11 The calculated $\langle u^2 \rangle$ of Na in 2% Na-vacant Na_3PS_4 in (i) unconstrained, (ii) frozen-host lattice, and (iii) frozen PS_4 rotation cases using NVT-MLMD at 600 K. In case(i), the PS_4 units are allowed to perform wiggling and rotation motion, while in case(ii) all the degree of freedom of host-lattice is frozen, in case(iii) the wiggling dynamics of PS_4 units are allowed. Hence by comparing the three cases, we can see that the wiggling dynamics of PS_4 also contributed significantly to Na-ion diffusion besides contributions from rotational dynamics (i.e., paddle-wheel mechanism).

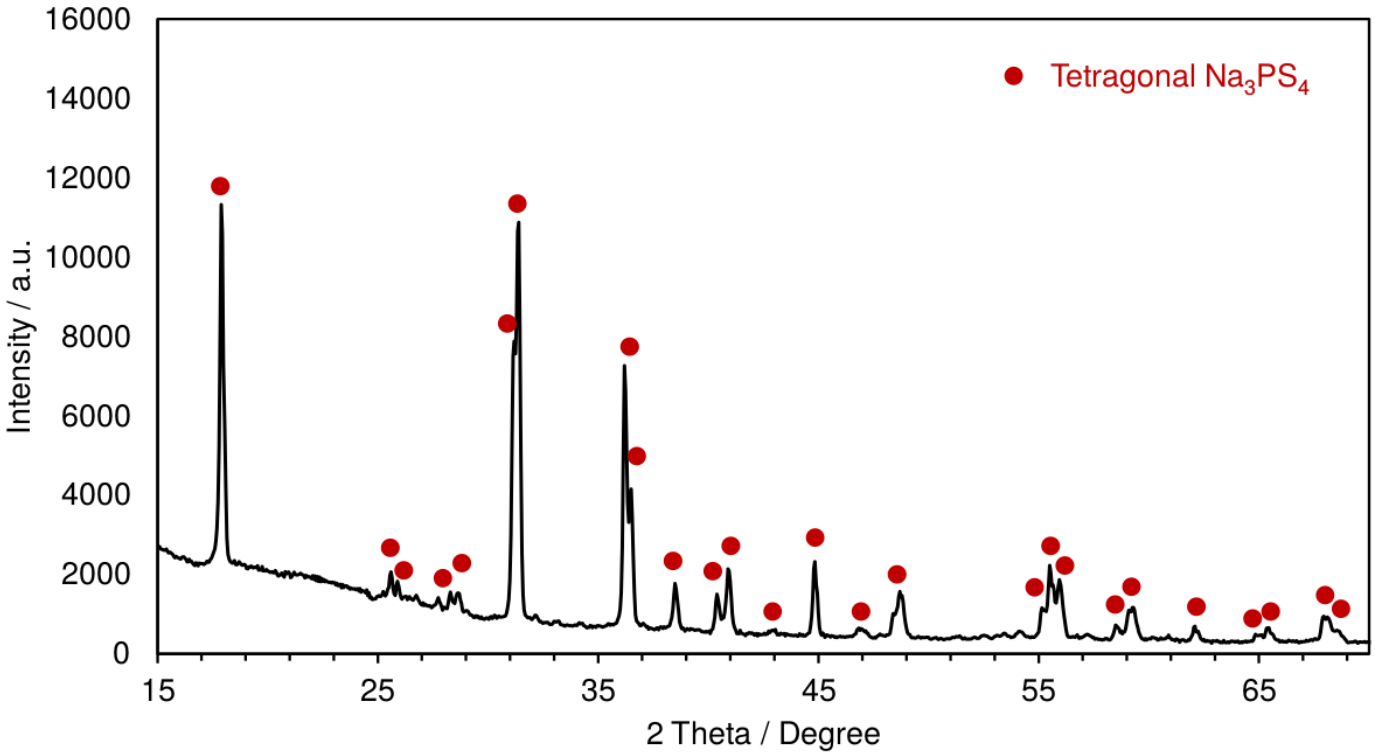

Figure S12 The measured diffraction pattern of Na_3PS_4at 300 K (tetragonal phase).

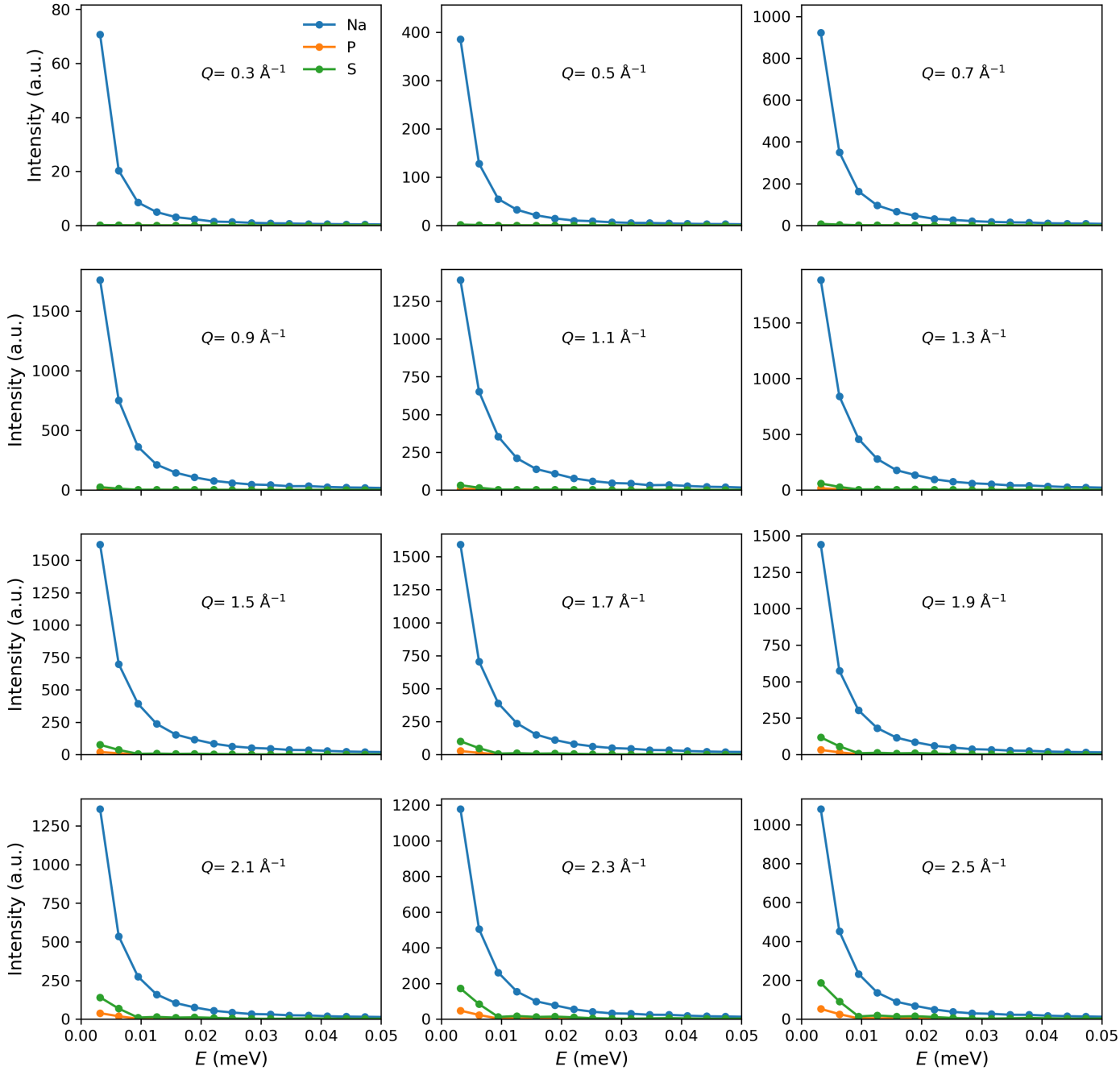

Figure S13 Simulated incoherent dynamical structure factor, $S_{inc}(Q,E)$ of Na, P and S at T=600 K.

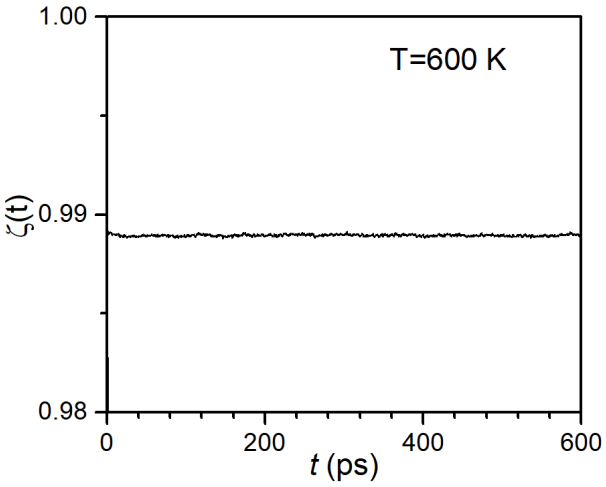

Figure S14 The calculated angular autocorrelation function ς (t), of PS_4 tetrahedral in Na_3PS_4 with 0.6% Na vacancies at T=600 K.

Notes and references