

## Supplementary Information

### Topology Driven and Soft Phonon Mode Enabled Na-ion Diffusion in Quaternary Chalcogenides, $\text{Na}_3\text{ZnGaX}_4$ (X=S, and Se)

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### Sample Preparation

$\text{Na}_3\text{ZnGaS}_4$  was synthesized through high temperature solid-state reaction taking stoichiometric ratio of elements by combining 1.5 mM of  $\text{Na}_2\text{S}$ , 1 mM of Zn, 1 mM of Ga and 2.5 mM of S in a carbon coated quartz ampoule. For the synthesis of selenide analogue ( $\text{Na}_3\text{ZnGaSe}_4$ ), we followed flux route synthesis involving 3 mM of  $\text{Na}_2\text{Se}_2$ , 1 mM of Zn, 1 mM of Ga and 2.5 mM of Se taken in a quartz ampoule.  $\text{Na}_2\text{Se}_2$  was synthesized through stoichiometric reaction between Na and Se in liquid ammonia and all other precursors were purchased from Alfa Aesar. The reactants were carefully loaded into the ampoules inside argon-filled glove box ( $\text{O}_2 < 0.5$  ppm,  $\text{H}_2\text{O} < 0.5$  ppm). The loaded ampoules were connected to an adapter to avoid any exposure to air while transferring out from the glove box and subsequently heat sealed under vacuum. The sealed ampoules were placed in a temperature-controlled furnaces and temperature was ramped up at a rate of 20 °C/h up to 750 °C and dwelled at that temperature for 120 hours followed by cooling down to room temperature at a rate of 35 °C/h. The  $\text{Na}_3\text{ZnGaS}_4$  ampoules were then taken inside glovebox and samples were recovered. The flux synthesized  $\text{Na}_3\text{ZnGaSe}_4$  was washed with *N, N* dimethylformamide (DMF) to remove the excess flux before transferring into the glove box. Note that several batches of ampoules were heated to generate ~5 grams of materials for neutron scattering experiments. The phase purity of the samples was evaluated by one-to-one comparison of experimental and simulated powder X-ray diffraction patterns of  $\text{Na}_3\text{ZnGaX}_4$  (X = S, Se) (see Figure S1).

## Powder X-ray Diffraction

Laboratory powder X-ray diffraction data were collected from a PANalytical X'Pert Pro diffractometer equipped with a Cu K $\alpha$  anode and a linear array PIXcel detector over a  $2\theta$  range of 5–90° with an average scan speed of 0.0472° S<sup>-1</sup>. The samples were hand ground into fine powder inside glovebox and transferred into airtight cells with the Kapton film to collect the data.

## Simulation Details of thermodynamical and transport properties

The velocity auto-correlation function of  $i^{\text{th}}$  atomic species  $Z_i(t)$ , which reveals the underlying nature of the dynamical processes, has been calculated using velocity trajectory  $\vec{v}_i(t)$ <sup>1</sup>

$$Z_i(t) = \frac{\langle \vec{v}_i(0) \cdot \vec{v}_i(t) \rangle}{\langle \vec{v}_i(0) \cdot \vec{v}_i(0) \rangle} \quad . \quad (\text{S1})$$

We have calculated the partial phonon density of states (PDOS)  $g_k(\omega)$  of  $k^{\text{th}}$  species via the Fourier transform of velocity auto-correlation function  $Z_k(t)$ <sup>1,2</sup>:

$$g_k(E) = \frac{1}{\hbar\sqrt{2\pi}} \int Z_k(t) e^{iEt/\hbar} dt \quad . \quad (\text{S2a})$$

The total PDOS  $g(E)$  can be obtained as

$$g(E) = \sum_k g_k(E). \quad (\text{S2b})$$

The neutron-weighted PDOS  $g^n(E)$  can be obtained as

$$g^n(E) = \sum_k \frac{\sigma_k}{M_k} g_k(E). \quad (\text{S2c})$$

Using the partial PDOS, we have computed the multiphonon contribution, which was further used to apply a multiphonon correction to the measured INS data. In the one-phonon neutron scattering approach and assuming the incoherent approximation, the relation between  $S(Q,E)$  and the partial phonon density of states  $g_k(E)$  can be expressed as

$$S(Q, E) = B \frac{Q^2 \{n(E,T)+1\}}{E} \sum_k \frac{\sigma_k}{M_k} e^{-2W_k(Q,T)} g_k(E) \quad (\text{S3})$$

where  $B$  is normalisation factor,  $\sigma_k$ ,  $M_k$ , and  $2W_k(Q,T)$  are the total neutron scattering cross-section, mass and Debye-Waller factor for atom  $k$ . The one-phonon and also multiphonon (up to 10 phonons)  $S(Q,E)$  spectra were calculated using the partial PDOS (obtained from time trajectories from the AIMD simulations), and finally the spectra were convoluted with the SEQUOIA resolution function for the incident energies used during the measurement using OCLIMAX (for details see refs<sup>3,4</sup>). The properly normalised calculated multiphonon spectra were subtracted from the experimental data, which then were transferred to  $g^n(E)$  by using equation (1) such that the results can be considered as the experimental neutron-weighted one-phonon density of states.

To investigate the local structure and cation ordering, the pair distribution function,  $g_{ij}(r)$ , among various atoms, has been calculated using the following relation<sup>5, 6</sup>,

$$g_{ij}(r) = \frac{1}{4\pi r^2 N_i N_j} \sum_{ii' \neq jj'}^{i'j'} \langle \delta(r - |\vec{r}_{ij}^{i'j'}(t)|) \rangle \quad (S4)$$

Where  $N_i$  and  $N_j$  are the total numbers of atoms of  $i^{th}$  and  $j^{th}$  species,  $\vec{r}_{ij}^{i'j'}(t)$  is the relative position between  $i^{th}$  number of atoms of  $i^{th}$  type and  $j^{th}$  number of atoms of  $j^{th}$  species at time  $t$ , and  $\langle \dots \rangle$  is the ensemble average.

We have also computed the mean square displacement (MSD),  $\langle u_i^2(t) \rangle$  from atomic trajectory using the following equation<sup>7</sup>

$$\langle u_i^2(t) \rangle = \frac{1}{N_i} \sum_{j=1}^{N_i} \langle |\vec{r}_i^j(t) - \vec{r}_i^j(0)|^2 \rangle \quad (S5)$$

where  $N_i$  is the total number of  $i$  type species and  $\vec{r}_i^j(t)$  is the position coordinate of  $j^{th}$  atom of  $i^{th}$  type species. Using the slope of the linear region of MSD vs.  $t$ (ps) plot, the diffusion coefficient has been estimated using Einstein's relation,

$$D = \frac{\Delta \langle u_i^2 \rangle}{6\Delta t} \quad (S6)$$

The self-Van-Hove correlation function,  $G_s(r, t)$ , which carries information on the evolution of atoms with time and space, has been computed using the following relation<sup>8, 9</sup>,

$$G_s(r, t) = \frac{1}{N} \sum_{i=1}^N \delta(r - (r_i(0) - r_i(t))) \quad (S7)$$

The total dynamical structure factor  $S_{total}(Q, E)$  for diffusive cations, where the majority of the scattering is dominated by incoherent scattering, was calculated using the following relation<sup>10, 11</sup>,

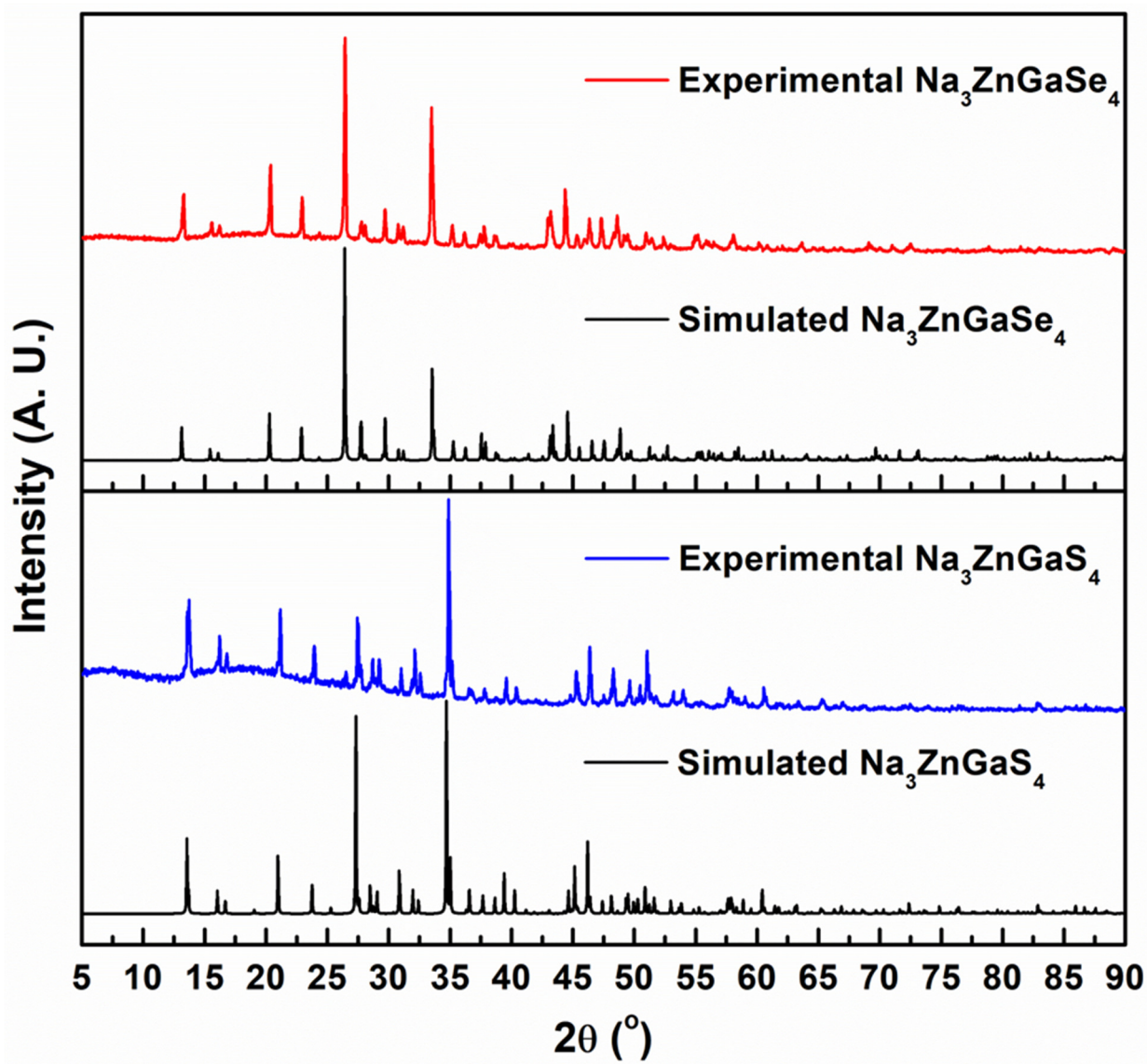
$$S_{total}(Q, E) = \sum (b_{coh}^i b_{coh}^j) S_{coh}^{ij}(Q, E) + \sum_i (b_{inc}^i)^2 S_{inc}^i(Q, E) \quad (S8)$$

where,  $b_{coh}^i$  and  $b_{inc}^i$  be the coherent and incoherent scattering length of  $i^{th}$  type of atoms and  $S_{coh}^{ij}(Q, E)$  represents coherent dynamical structure factor.

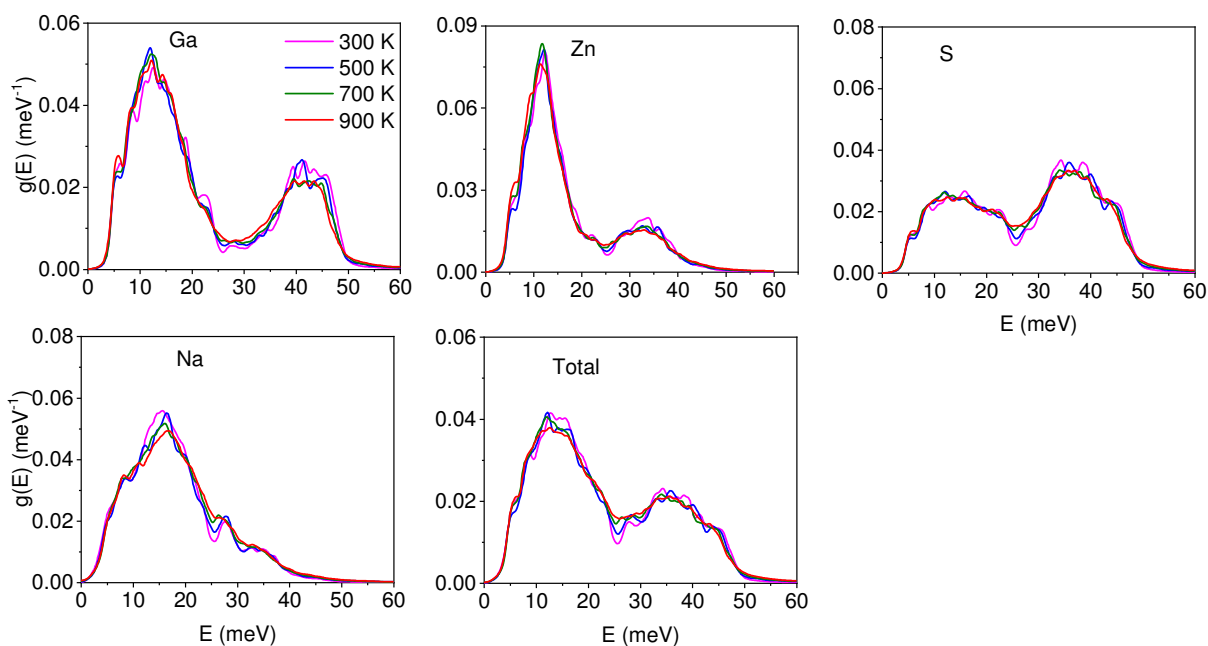
**TABLE S1:** The close interatomic contacts for Na atoms at  $32g$  and  $16f$  sites in  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) are tabulated below. The room temperature lattice parameters of  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}/\text{Se}$ ) are  $a = b = 12.925/13.43 \text{ \AA}$  and  $c = 18.623/19.15 \text{ \AA}$ . For S compound, the close Na-Na contacts formed by  $32g$ - $32g$  sites are  $3.17 \text{ \AA}$  and  $4.07 \text{ \AA}$  in the  $a$ - $b$  plane while a close contact of  $4.17 \text{ \AA}$  is along the  $c$ -axis. The corresponding close Na-Na distances for Se compound are  $3.36 \text{ \AA}$  and  $4.17 \text{ \AA}$  in the  $a$ - $b$  plane while a close contact of  $4.59 \text{ \AA}$  can be found along the  $c$ -axis.

<b><math>\text{Na}_3\text{ZnGaS}_4</math></b>		<b><math>\text{Na}_3\text{ZnGaSe}_4</math></b>	
Interatomic distances ( $\text{\AA}$ )	Na-Na	Interatomic distances ( $\text{\AA}$ )	Na-Na
3.17	$32g$ - $32g$	3.36	$32g$ - $32g$
3.81	$32g$ - $16f$	3.93	$32g$ - $16f$
3.85	$32g$ - $16f$	4.03	$32g$ - $16f$
4.07	$32g$ - $32g$	4.17	$32g$ - $32g$
4.12	$32g$ - $16f$	4.38	$32g$ - $16f$
4.25	$16f$ - $16f$	4.47	$16f$ - $16f$
4.17	$32g$ - $32g$	4.59	$32g$ - $32g$

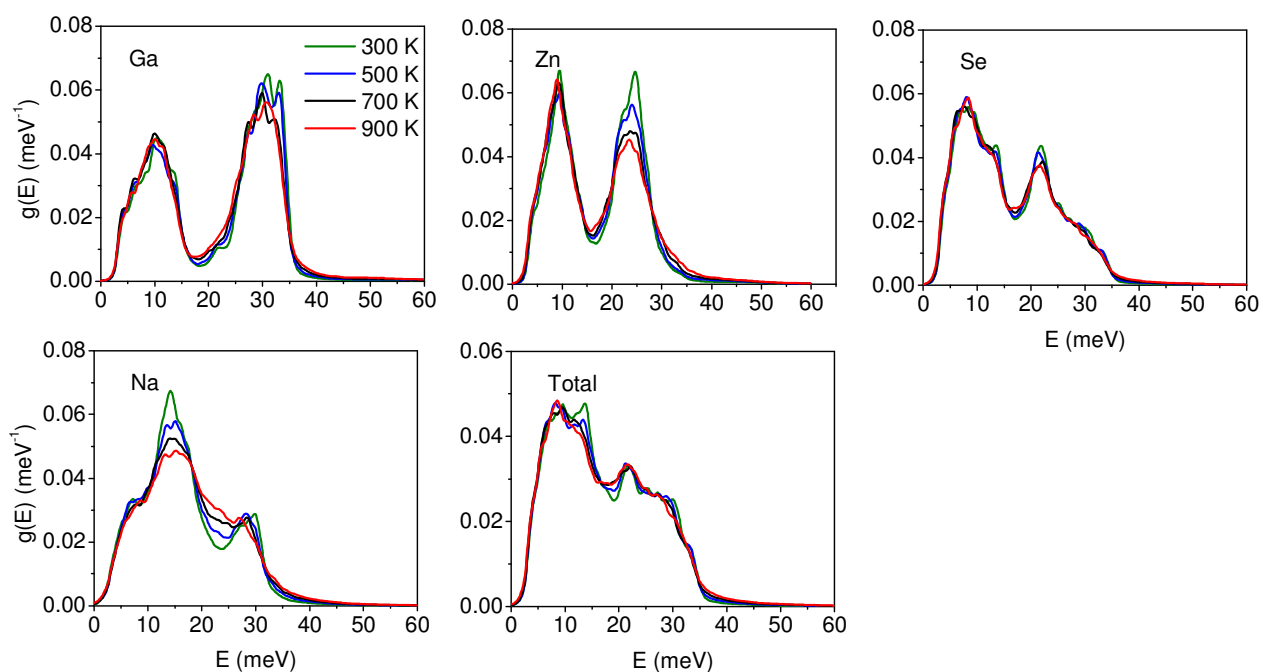
**Figure S1.** The experimental Powder X-ray diffraction patterns of  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) showing good matching with the simulated powder patterns generated from single-crystal atomic coordinates. The X-ray wavelength was  $1.5418 \text{ \AA}$ .



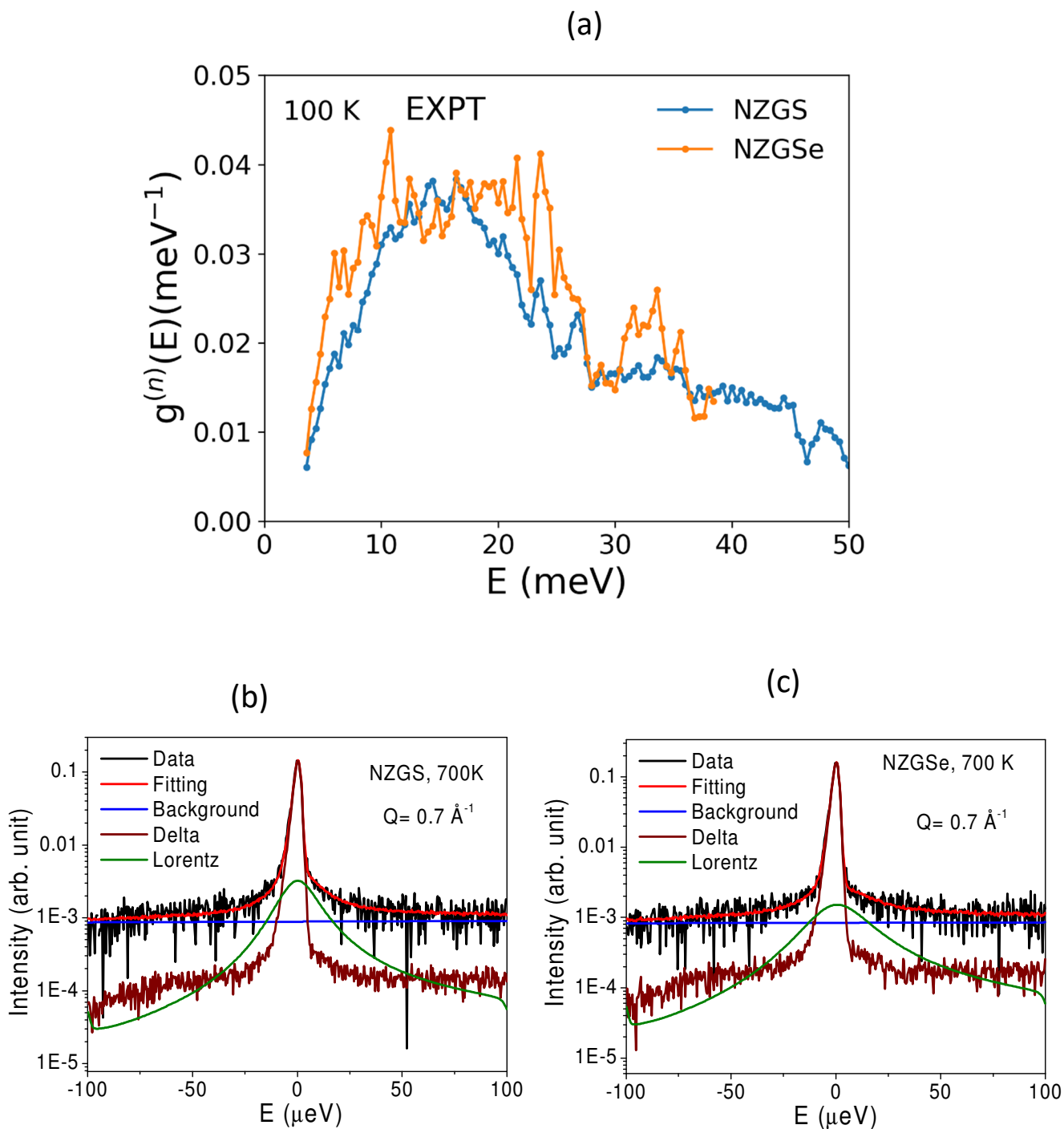
**Figure S2 (a).** The calculated phonon density of states in  $\text{Na}_3\text{ZnGaS}_4$  with 2% Na-vacancy at various temperature using AIMD.



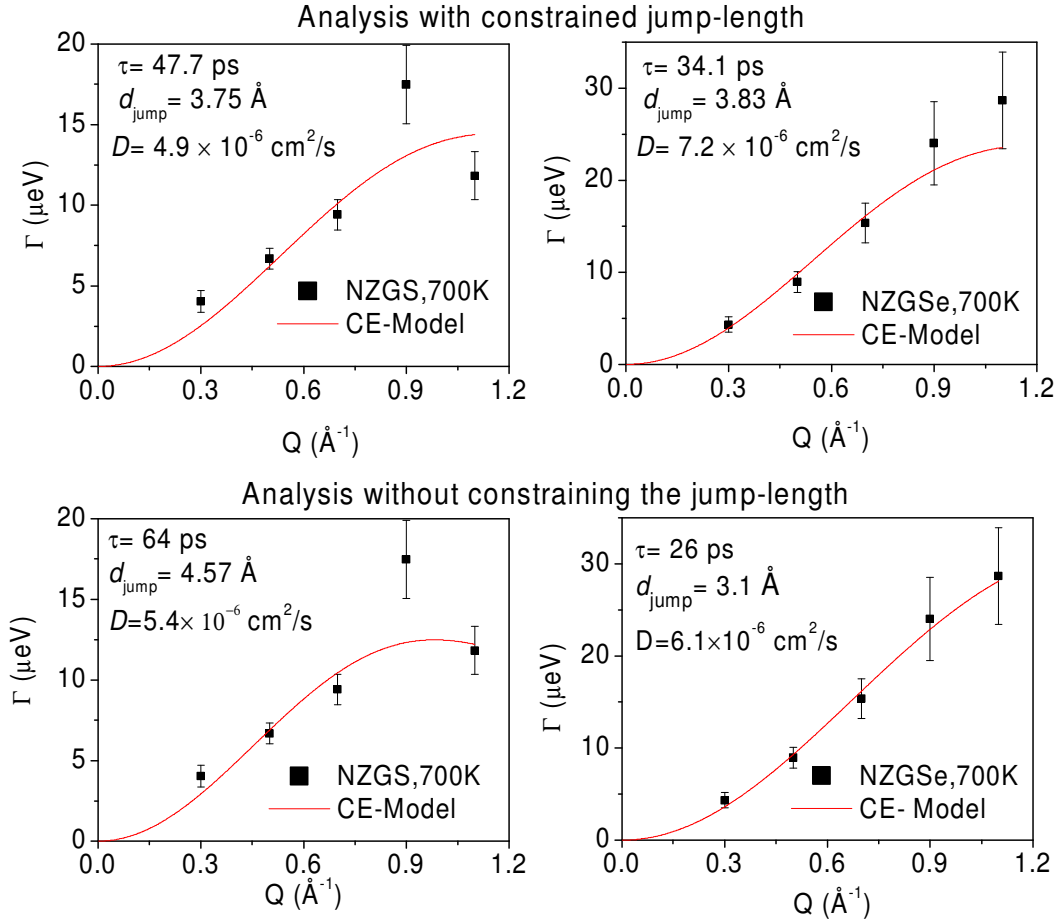
**Figure S2 (b).** The calculated phonon density of states in  $\text{Na}_3\text{ZnGaSe}_4$  with 2% Na vacancy at various temperature using AIMD.



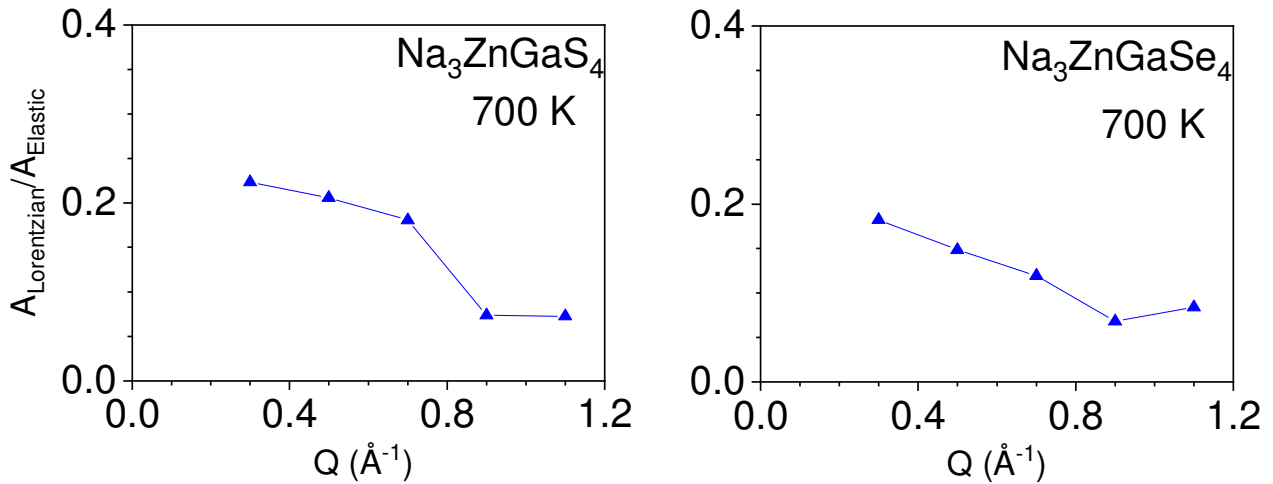
**Figure S3.** (a) The measured PDOS spectra for  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) at 100 K with an incident neutron energy of 82.9 meV. (b-c) The measured QENS spectra are fitted with one Lorentzian and delta function for both the chalcogenide compounds  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) at 700 K.



**Figure S3 (d)** Analysis of the QENS data of  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) compounds using at 700 K, using C-E model (red solid line). (Upper Panel) With constraining the jump-length ( $d$ ) obtained from AIMD simulation as a parameter and (Lower Panel) without constraining the jump length.

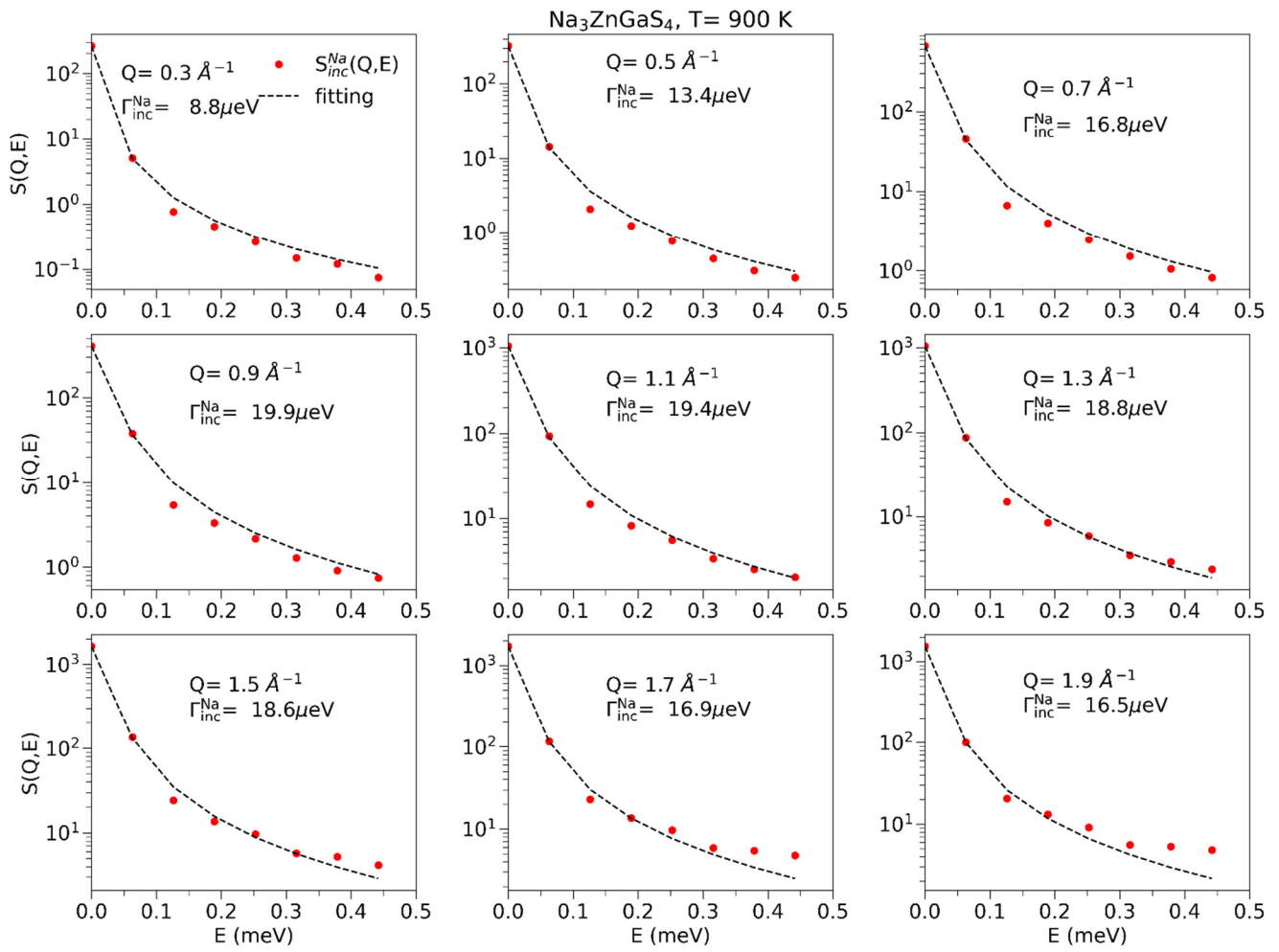


**Figure S3 (e).** The relative spectral weight of the quasielastic area ( $A_{\text{Lorentzian}}$ ) with respect to elastic component ( $A_{\text{Elastic}}$ ) as a function of  $Q$  in both chalcogenide compounds ( $\text{Na}_3\text{ZnGaS}_4$ , and  $\text{Na}_3\text{ZnGaSe}_4$ ) at 700 K.

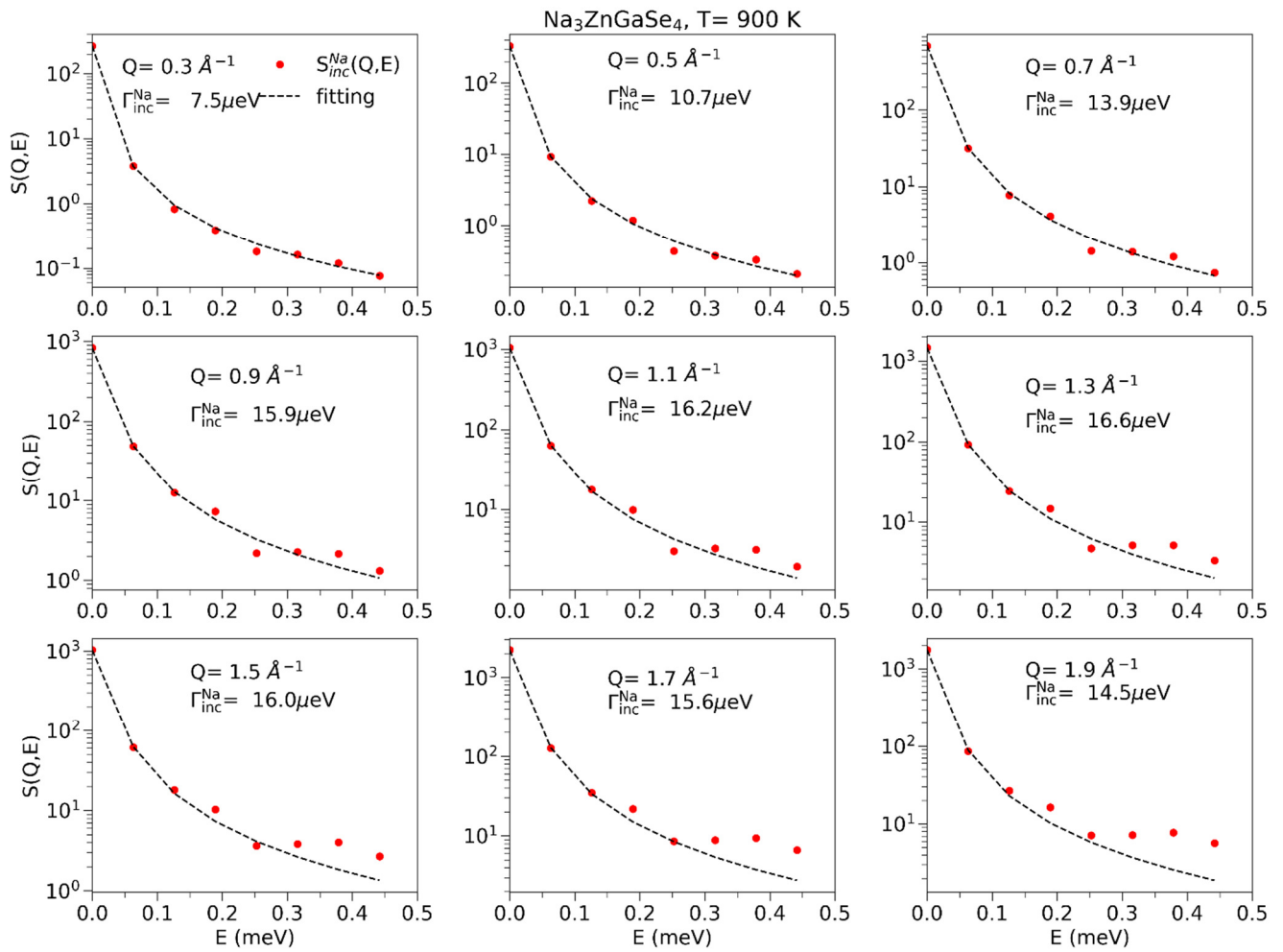




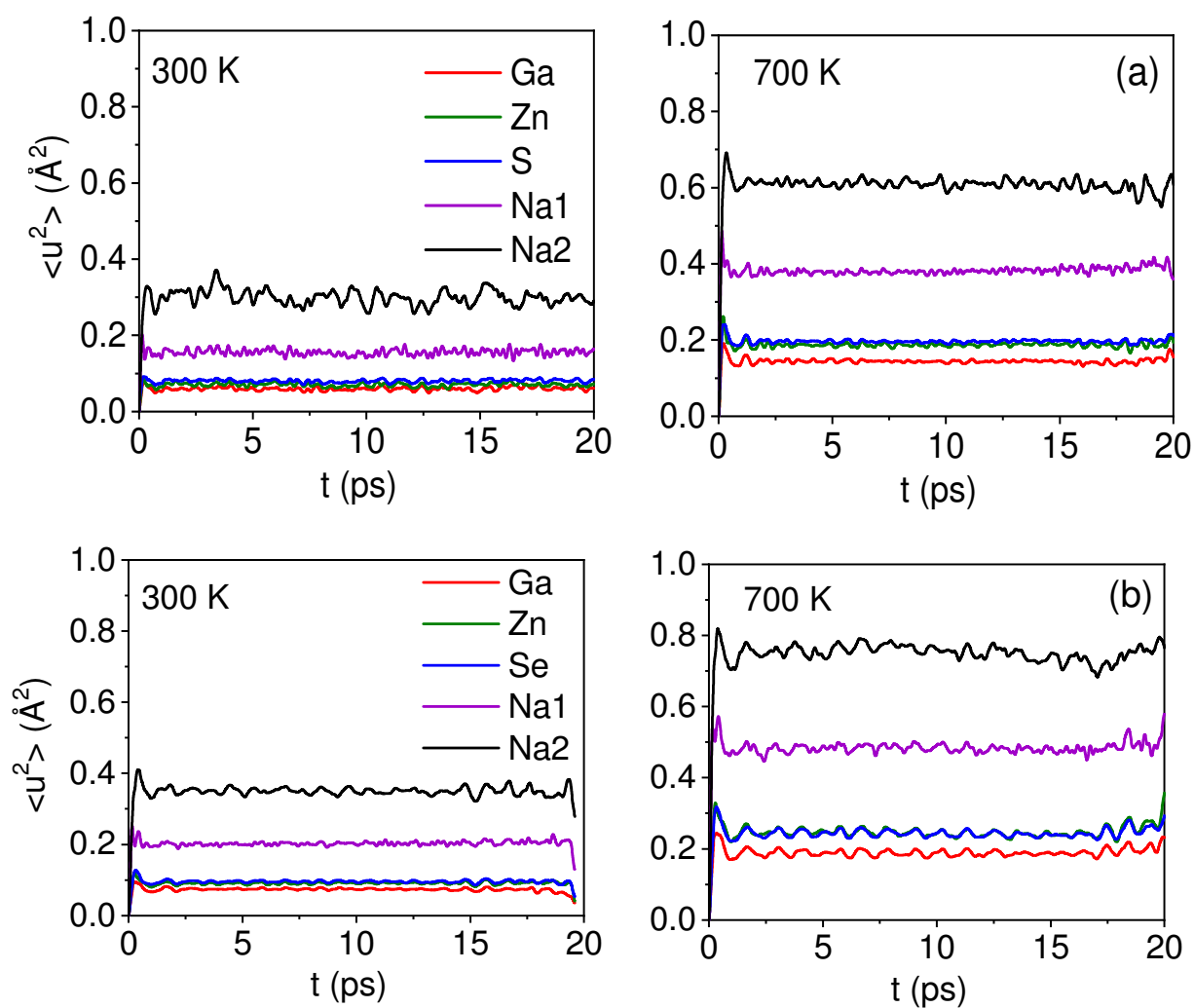
**Figure S4.** The calculated  $S(Q, E)$  of Na-ion in the 2% Na-deficit structure of  $\text{Na}_3\text{ZnGaS}_4$  at 900 K using AIMD.



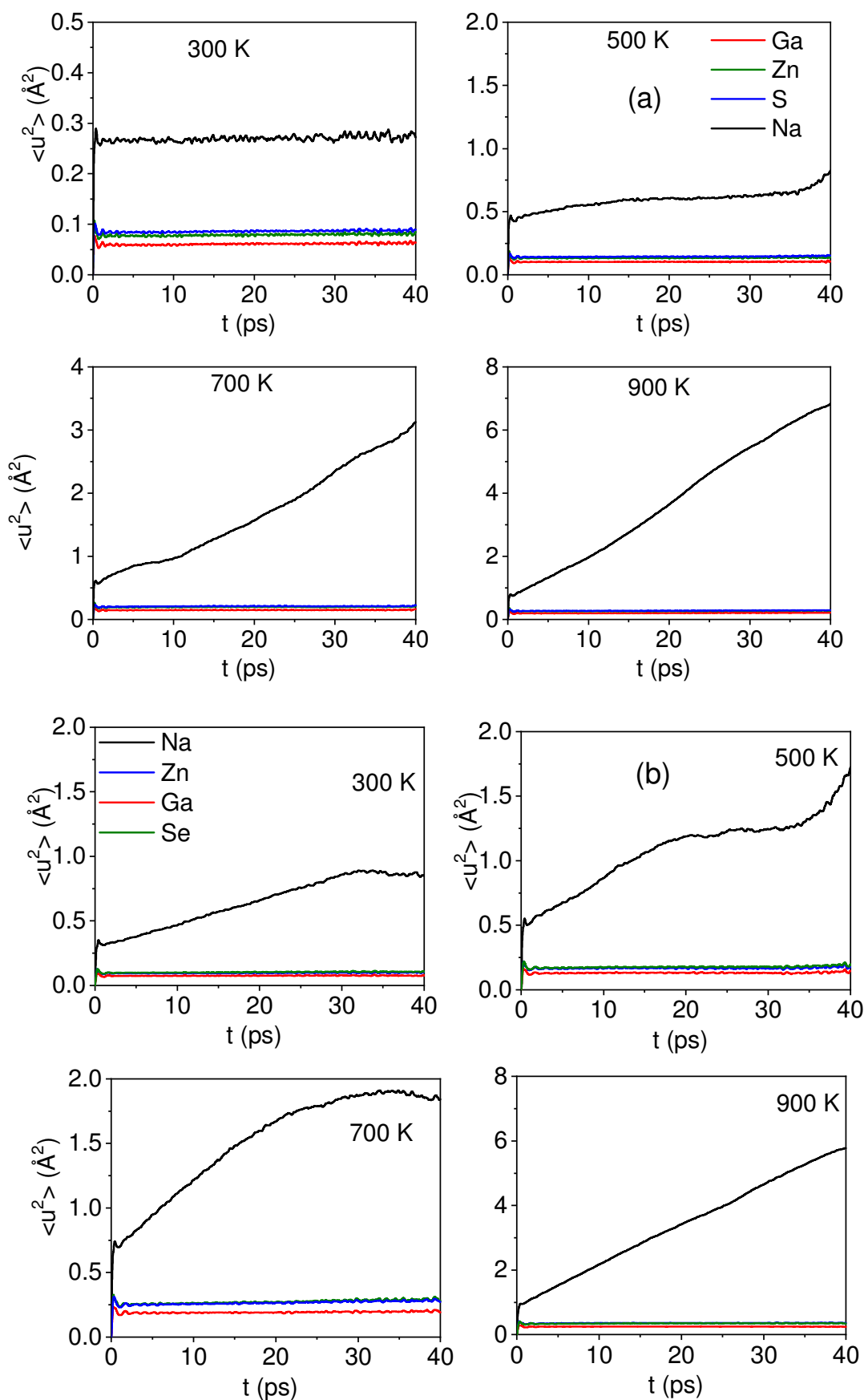
**Figure S5.** The calculated  $S(Q, E)$  of Na-ion in the 2% Na-deficit structure of  $\text{Na}_3\text{ZnGaSe}_4$  at 900 K using AIMD.



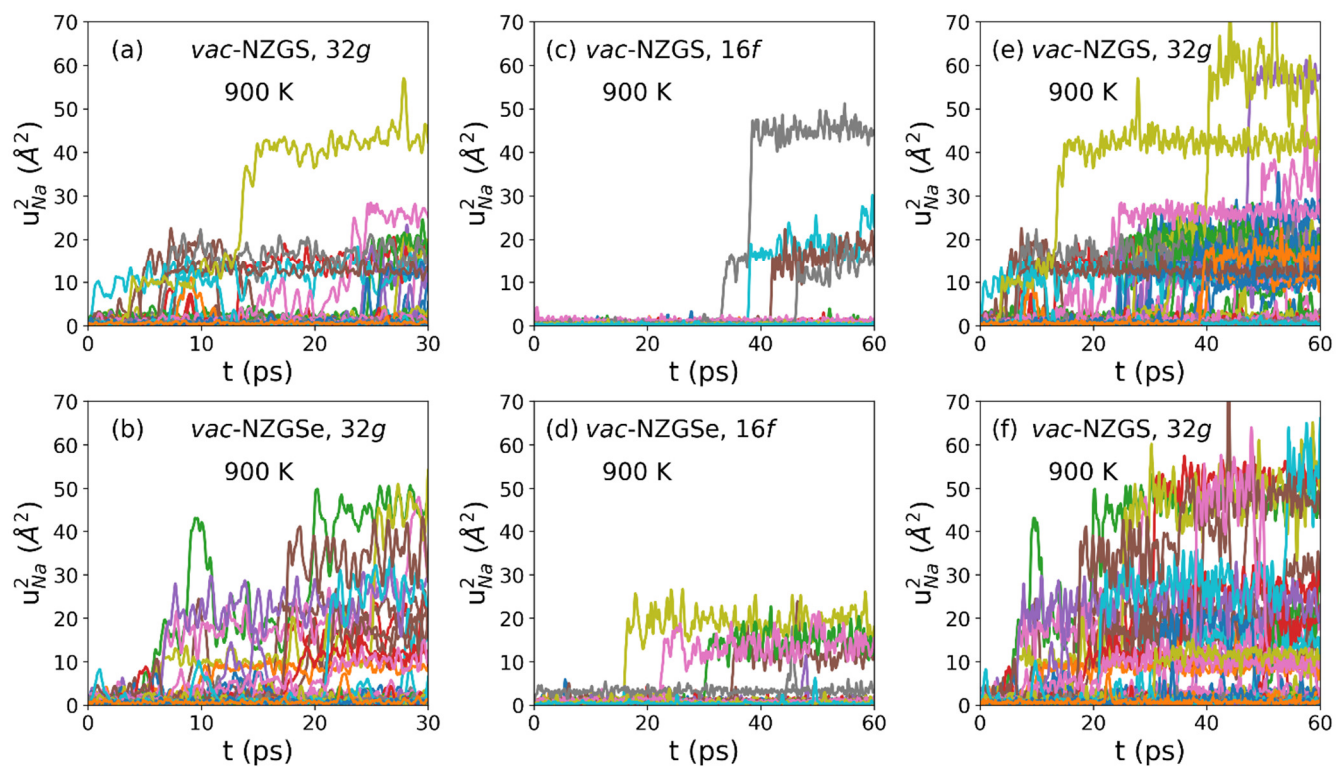
**Figure S6.** (a) The calculated MSD in stoichiometric  $\text{Na}_3\text{ZnGaS}_4$  at two temperatures using AIMD. (b) The calculated MSD in stoichiometric  $\text{Na}_3\text{ZnGaSe}_4$  at two temperatures using AIMD.



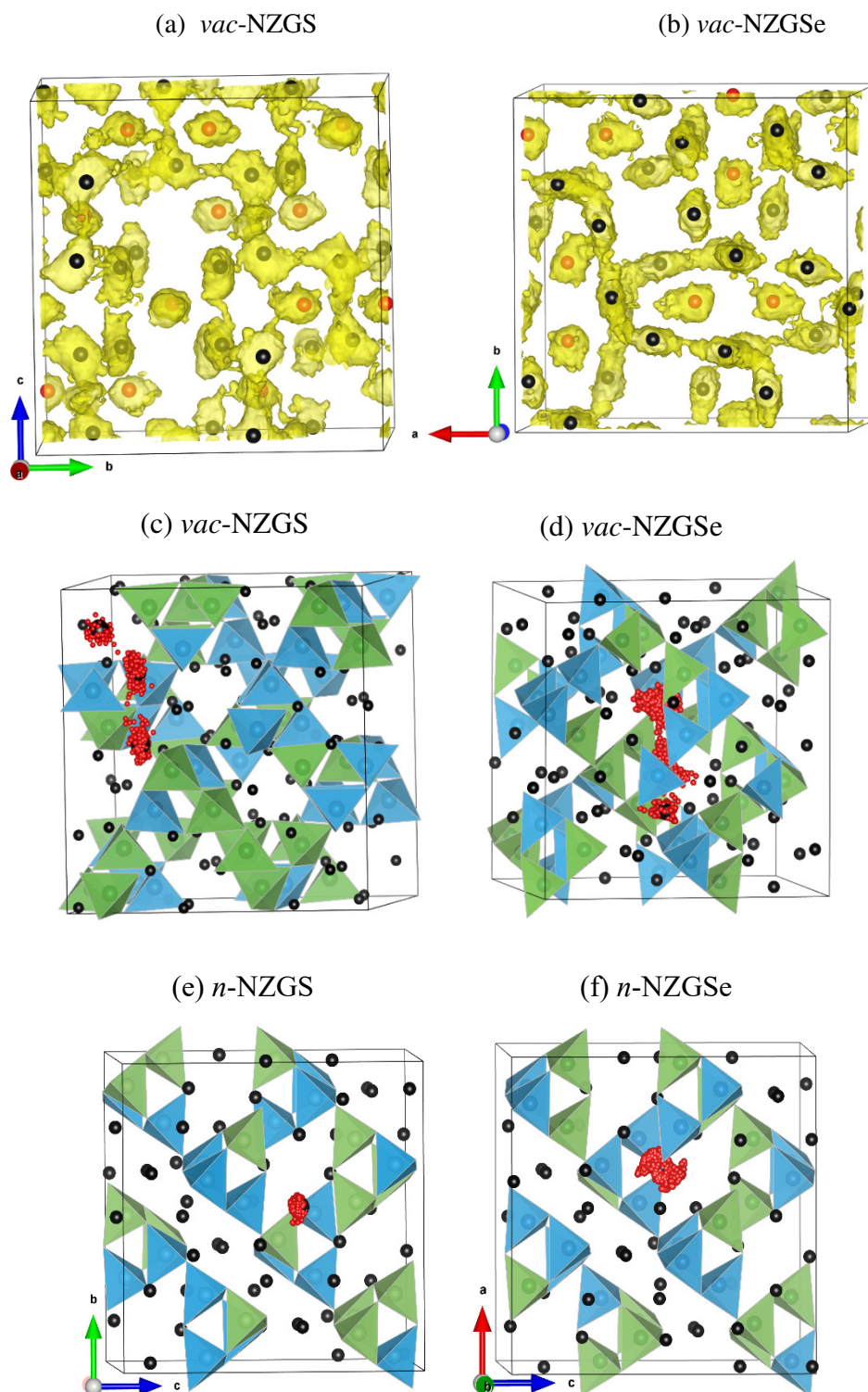
**Figure S7.** (a) The calculated MSD in the 2% Na-deficit structure of  $\text{Na}_3\text{ZnGaS}_4$  at various temperatures using AIMD. (b) The calculated MSD in the 2% Na-deficit structure of  $\text{Na}_3\text{ZnGaSe}_4$  at various temperatures using AIMD.



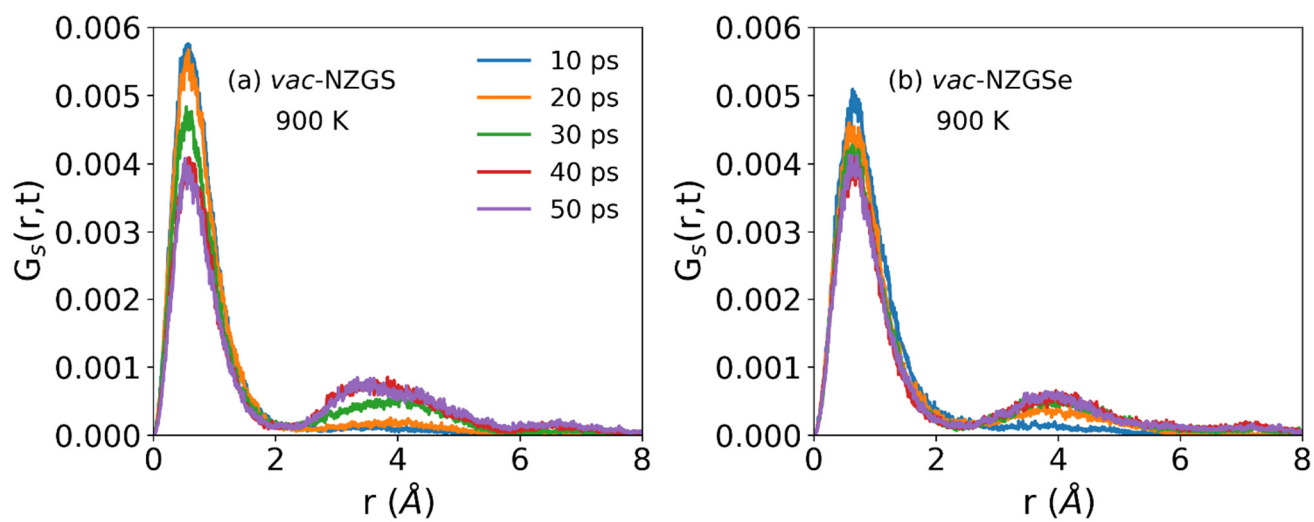
**Figure S8.** The calculated squared displacements ( $u^2$ ) of individual Na atoms at  $32g$  and  $16f$  Wyckoff sites at 900 K in  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ).



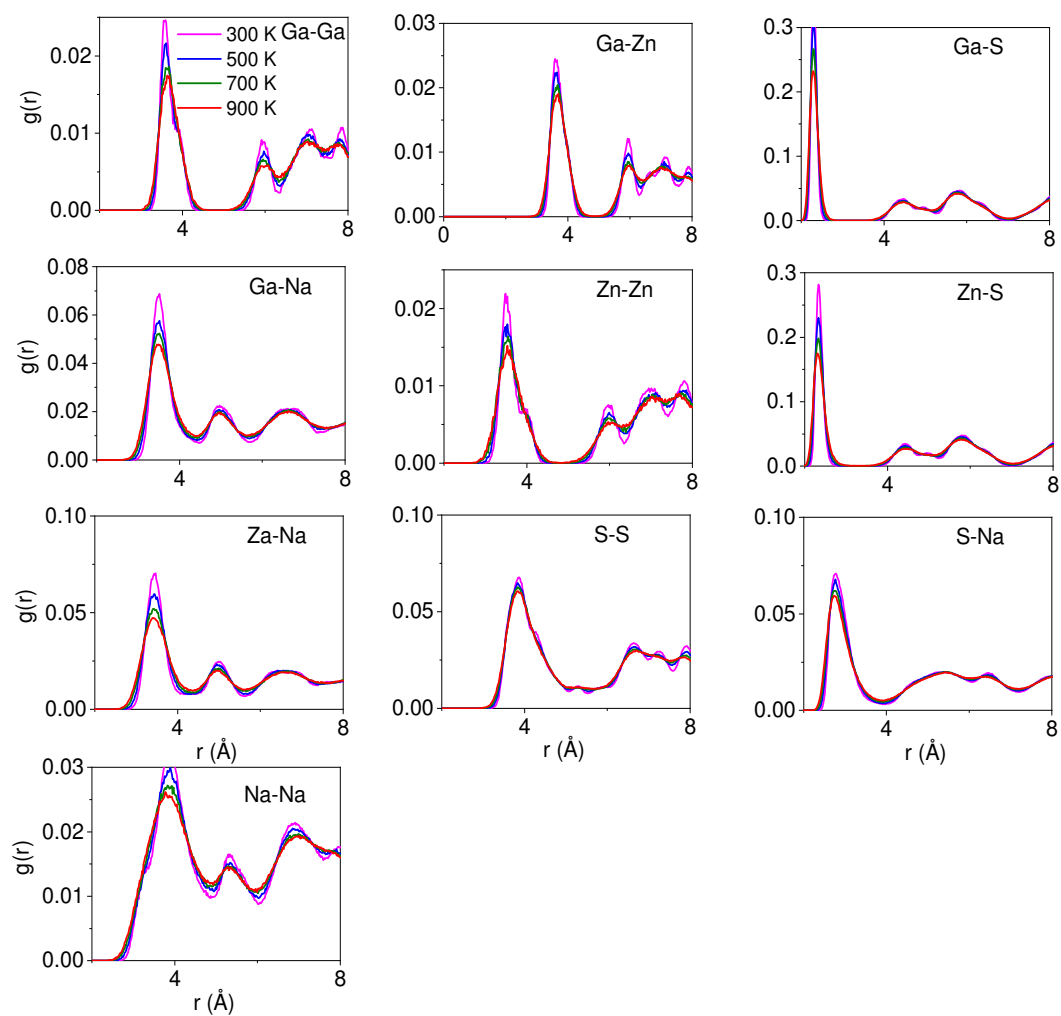
**Figure S9.** (a, b) The calculated Na-occupation probability with isosurface value  $\sim 0.001/\text{\AA}^3$  in the 2% Na-deficit structure of  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) at 900 K using AIMD. The  $32g$  ( $\text{Na}_2$ ) Wyckoff sites Na atoms are shown by black solid sphere and  $16f$  ( $\text{Na}_1$ ) Wyckoff sites Na atoms shown by red sphere. (c, d) The calculated atomic trajectory in the 2% Na-deficit structure of  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) compounds for 60 ps with 120 fs intervals at 900 K using AIMD and (e, f) and also in stoichiometric  $\text{Na}_3\text{ZnGaX}_4$  ( $X=\text{S}, \text{Se}$ ) compounds for 20 ps with 40 fs intervals at 700 K. We have shown only half of the unit cell boundary along the a-axis for clarity. (c-f) The Na atoms are shown by black spheres. The  $\text{ZnX}_4$  and  $\text{GaX}_4$  polyhedral units are shown by green and blue colors, respectively. The Na time-dependent trajectory is shown by small red spheres.



**Figure S10.** The calculated self Van-Hove correlation function in *vac*-NZGS and *vac*-NZGSe for 50 ps with 10 ps time intervals at 900 K using AIMD.

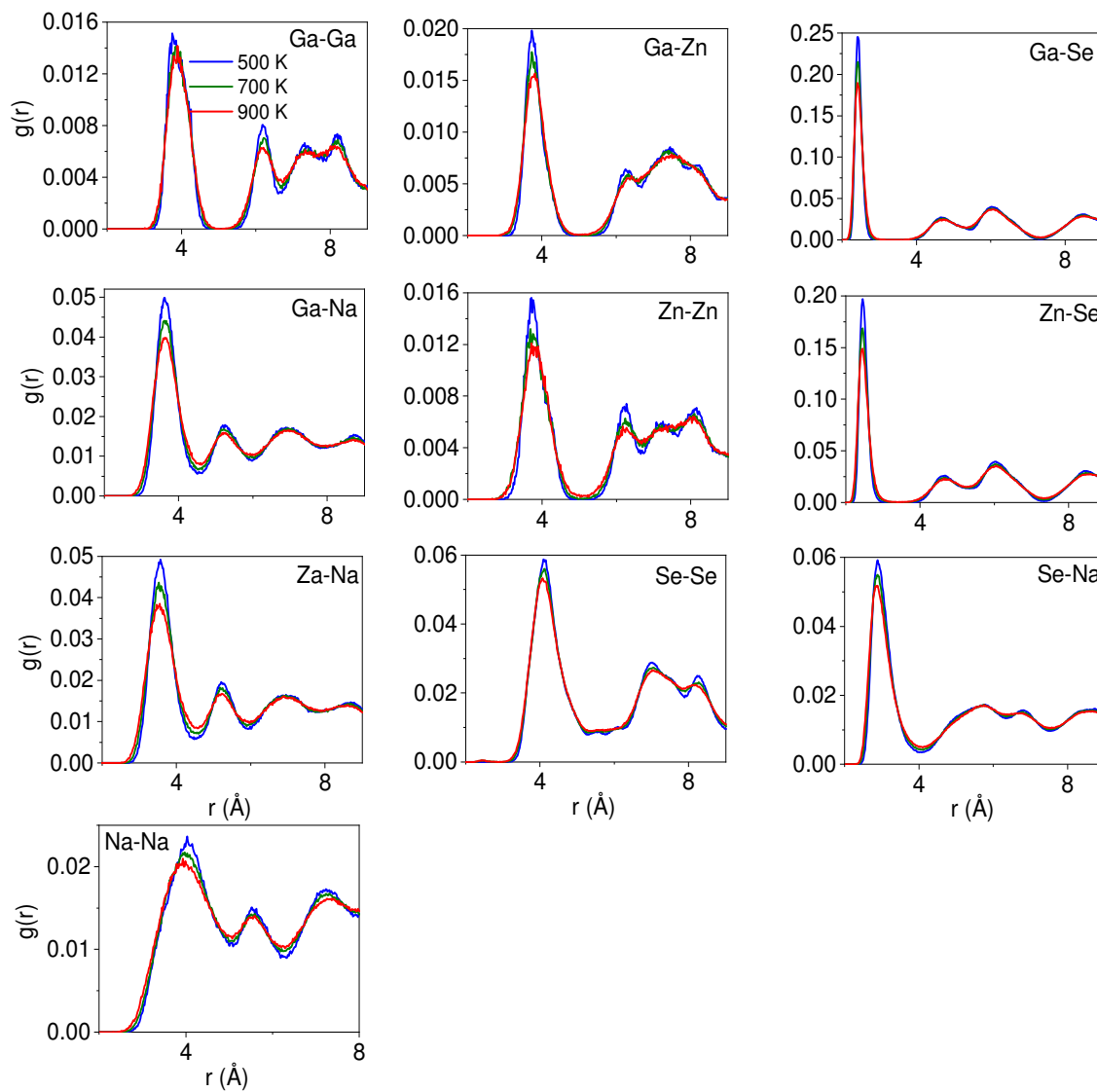


**Figure S11 (a).** The calculated pair distribution function in the 2% Na-vacancy structure of  $\text{Na}_3\text{ZnGaS}_4$  at various temperatures using AIMD.





**Figure S11 (b).** The calculated pair distribution function in the 2% Na vacancy structure of  $\text{Na}_3\text{ZnGaSe}_4$  at various temperatures using AIMD.



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