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Electronic Supporting Information

Direct Atomic-scale Observation of Ag^+ Diffusion Structure in the Quasi-2D "Liquid-like" State of Superionic Thermoelectric $AgCrSe_2$

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Sec. 1: Specific heat C_V

We estimated the bulk specific heat C_V from C_P using following equation:[S1]

$$C_V = C_P - 9\alpha^2 BVT \tag{S1}$$

where α is the thermal expansion coefficient, B the bulk modulus, V the volume per atom. C_P was determined by the comparative laser flash method and the results were reported elsewhere.[S2] The thermal expansion coefficient α is taken from Ref. S3 and a value of ~2.0×10^{-5} K^{-1} is used. The bulk modulus B is calculated from the experimental sound speed to be ~57.8 GPa. Given these values, the calculated C_V is shown in **Figure S1** as circles and it follows the Dulong-Petit limit $3Nk_B$=0.314 J g^{-1} K^{-1} fairly well.

In comparison, we also calculate the theoretical temperature-dependent C_V by extrapolating the thermal properties from the ground state within the DFT quasi-harmonic approximation (QHA).[S4] Note that the contribution owing to order-to-superionic phase transition is not taken into consideration in DFT QHA calculation. The result is presented in Figure S1 as solid line and it is also in good agreement with experiments. It is thus implied that the phonon vibrations and diffusion are virtually decoupled.

Sec. 2: Sound speed measurements

The speed of sound was measured by the ultrasonic pulse-echo approach using an Olympus 5037PR pulse/receiver. The echoes were recorded by a 5 MHz transducer and displayed on a Tektronix MDO3054 digital oscilloscope. The measured sound speed of transverse and longitudinal modes v_T and v_L at room temperatures are 1783.4 m·s^{-1} and 3651.1 m·s^{-1}, respectively. The mean sound speed $\bar{v}_s$ is calculated by v_T and v_L:

$$\bar{v}_s^3 = \frac{3}{2v_T^{-3} + v_L^{-3}} \tag{S2}$$

and a value of ~2003.3 m·s^{-1} can be obtained.

Sec. 3: κ_l of disorder solids

According to Ref. S5, the lower limit of κ_l for a disorder or amorphous solid can be analytical expressed by the following integrals:

$$\kappa_{l,a} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \tag{S3}$$

where the sum is taken over the two transverse and one longitudinal waves with sound speed v_i; Θ_i is the Debye temperature for each mode: $\Theta_i = v_i(\hbar/k_B)(6\pi^2 n)^{1/3}$ and n is the number density of atoms. Provided the experimental sound speed and n=4.8×10^{28} m^{-3} of AgCrSe$_2$, the high temperature limit of $\kappa_{l,a}$ ($T \rightarrow +\infty$) can be calculated as ~0.53 W m^{-1} K^{-1}.

Sec. 4: Relaxation time τ of diffusion and the critical temperature T_{cr} for TA phonon suppression

The relaxation time τ of ion diffusion in solids usually obeys Arrhenius relation [Equation (3)]. The prefactor, or the attempt frequency τ_0^{-1} for the diffusion in monatomic or cubic crystals was studied theoretically based on lattice dynamics.[S6, S7] It was shown that τ_0^{-1} can be related to average Debye frequency cutoff ω_D in a simple way, e.g. $\tau_0^{-1} = \left(\frac{3}{5}\right)^{\frac{1}{2}} \omega_D$ for monatomic crystals and $\tau_0^{-1} \approx 0.65\omega_D$ for cubic crystals. This limit of τ_0^{-1} is simply because diffusive motion is thermally activated and its frequency cannot exceed the maximum allowed frequency of the whole system. Rice *et al.* calculated τ_0^{-1} for a number of monatomic crystals, e.g. Cu, Ag, Au, Al and found that there is a remarkable agreement between τ_0^{-1} and ω_D: $\tau_0^{-1} \approx \omega_D$.[S8] Hence, we relate τ_0^{-1} and ω_D in a simple way that $\tau_0^{-1} = s\omega_D$ and s is a variable that depends on atom configurations and crystal structures. For AgCrSe$_2$, the average Debye frequency is determined to be ~2.49 THz by the average sound speed $\bar{v}_s$~2003.3 m·s^{-1}. If $s = 1$, we have τ_0=0.4 ps.

Alternatively, it was proposed that τ_0^{-1} could also be obtained by the activation energy E_a:[S8]

$$\tau_0^{-1} = \frac{1}{a_0}\sqrt{2E_a/M} \tag{S4}$$

where a_0 is the hopping distance and M the ionic mass. Using the reported E_a value ~0.11 eV[S9] and a hopping distance a_0=2.2 Å between *α*- and *β*-sites, τ_0 of Ag^+ ions is calculated to be ~0.5 ps, which is in perfect agreement with the estimation by $\tau_0^{-1} = \omega_D$. It's interesting to remark that τ_0^{-1} is usually at the high frequency end of ω_D or the phonon spectrum, which implies that diffusion is mainly driven by the high energy optical phonon modes. As a result, a strong coupling between diffusion and optical phonon might occur and should be easily identified in phonon dispersion or density of states. In fact, it was found that specific phonon modes dominated by Cu ions break down in the isostructure system $CuCrSe_2$ due to diffusion.[S10]

Although the diffusion is mainly driven by optical phonon, its frequency is not practically high enough to effectively suppress the low energy phonon modes. Only at extremely high temperature, the relaxation time τ for diffusive motion approaches τ_0 and it is expected that at certain critical temperature T_{cr} diffusion would compete with the low-lying TA phonon modes. T_{cr} can be directly calculated by Equation (5), which corresponds to $\omega_{TA}\tau_c = 1$. The most straightforward way to reduce T_{cr} is to reduce E_a. Another possible means to reduce T_{cr} is to increase ω_D/ω_{TA}. We can rewrite ω_D/ω_{TA} by the expression of ω_D:

$$\frac{\omega_D}{\omega_{TA}} = \frac{\bar{v}_s}{\omega_{TA}}(6\pi^2 n)^{1/3} \tag{S5}$$

For simplicity, it is assumed that $\omega_{TA} = k_{ZB}v_T$, where k_{ZB} is the maximum wave vector at the zone boundary. Inserting Equation (S2) and the relation $\omega_{TA} = k_{ZB}v_T$ back into Equation (S5), we now have

$$\frac{\omega_D}{\omega_{TA}} = \frac{(6\pi^2 n)^{1/3}}{k_{ZB}}\left[\frac{3}{2 + \left(v_T/v_L\right)^3}\right]^{1/3} \tag{S6}$$

Thus, ω_D/ω_{TA} is approximately proportional to the cell size (~ $1/k_{ZB}$) and it's predicted that larger system will have smaller T_{cr}. A smaller v_T/v_L ratio could also potentially increase ω_D/ω_{TA} but its effect is relatively weaker. A search for such materials and understanding the possible strong coupling between diffusion, low energy acoustic phonon and high energy optical phonon in these systems will be the scope of our future work.

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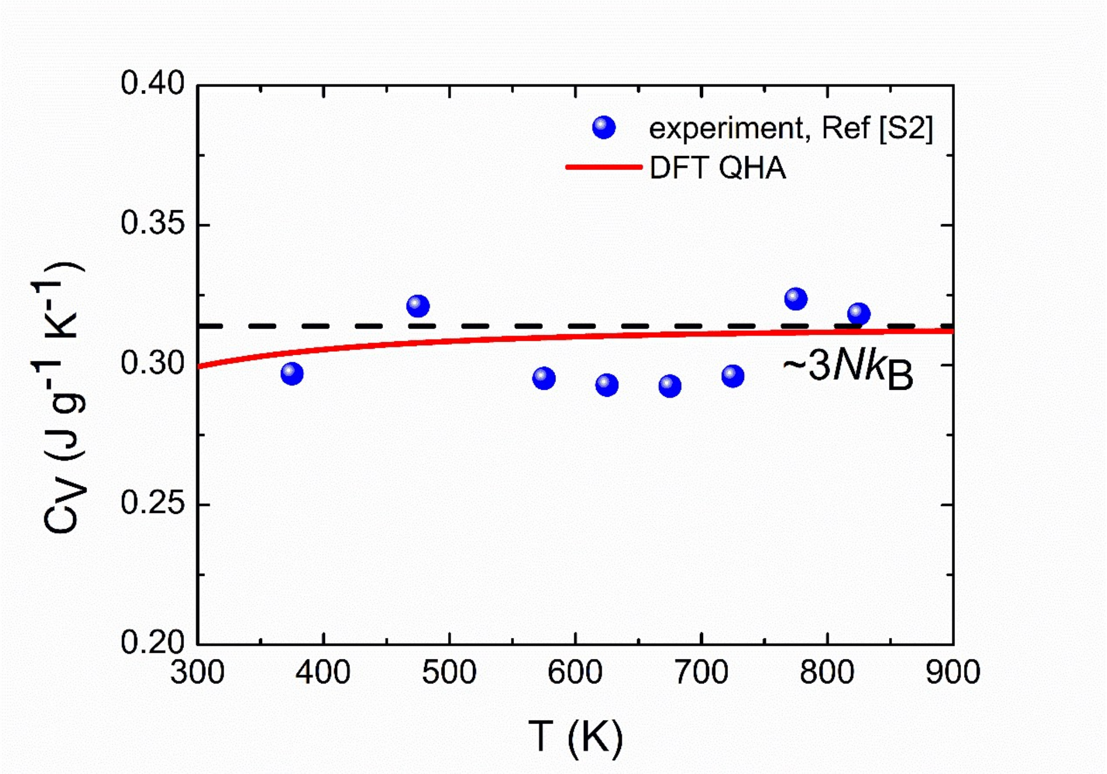

Figure S1. Experimental (circles)[S2] and calculated (solid line) specific heat C_V. Both values are close to the Dulong-Petit limit $3Nk_B$=0.314 J g^{-1} K^{-1} (dash line).