How dopants limit the ultrahigh thermal conductivity of boron arsenide: a first principles study - Supplementary Information

Mauro Fava,[1] Nakib Haider Protik,[2] Chunhua Li,[3] Navaneetha Krishnan Ravichandran,[4] Jesús Carrete,[5] Ambroise van Roekeghem,[1] Georg Madsen,[5] Natalio Mingo,[1] and David Broido[3]

[1]*LITEN, CEA-Grenoble, Grenoble, 38054, France*
[2]*John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA*
[3]*Department of Physics, Boston College, Chestnut Hill, MA 02467, USA*
[4]*Department of Mechanical Engineering, Indian Institute of Science, Bangalore, India*
[5]*Institute of Materials Chemistry, TU Wien,Vienna, A-1060, Austria*

(Dated: March 1, 2021)

I. SUPPLEMENTARY NOTES

A. Supplementary note I: V_K Scattering

Supplementary Figure 1 shows the V_K - only scattering rates at the concentration of $3.26 \cdot 10^{18}$ cm^{-3}. The frequency range between 4 and 8 THz is highlighted as it is relevant for the transport in the pristine boron arsenide. The plots show that (i) the phonon scattering rates are consistently larger for bond distortions involving C, Si and Ge impurities in their neutral states compared with those in their charged states, and (ii) Si_{As}, Ge_{As} and C_B dopants lead to noticeably weaker bond defect scattering than do C_{As}, Si_B and Ge_B. Since Ge and C also result in weak small mass differences when replacing host atoms As and B, the plots confirm the unusually weak total phonon-defect scattering rates for Ge_{As} and C_B dopants.

B. Supplementary note II: Hole Concentration

Supplementary Figure 2 we present the hole concentration with and without considering the compensation by donor impurities, in the stable As-rich growth conditions. It can be noted that the maximum hole doping is achieved in the case of Si impurities ($p > 10^{18}$ cm^{-3}), with the Ge case closely following. In the case of C defects the maximum of the hole concentration stabilises near 10^{17} cm^{-3}, i.e. one order of magnitude smaller, in virtue of its larger ionisation energy with respect to Si and Ge.

C. Supplementary note III: Frequency Shift

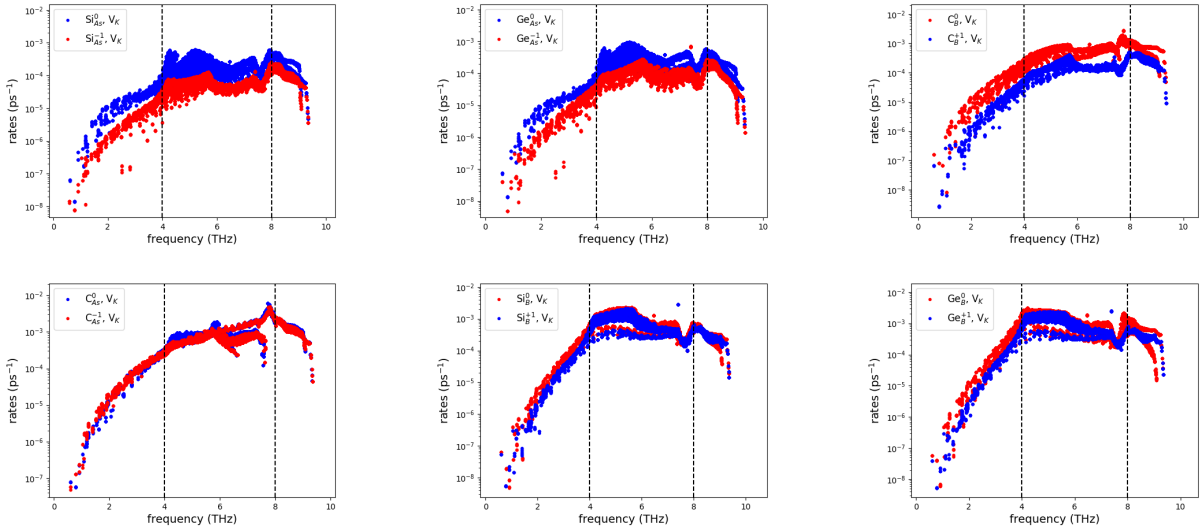
Point defects are a source of scattering and affect the lifetimes of phonons, but they can also potentially lead to a frequency renormalisation. While the latter is important in alloying conditions, here we show that its effect can be safely neglected for our purposes. To quantify the shift in the phonon frequencies we consider, in terms of the retarded Green's function G_0^+ of the the pristine system [1]:

$$\Omega_\lambda^2 = \omega_\lambda^2 + \chi \Re\left[\frac{\langle\lambda| T^+ |\lambda\rangle}{\langle\lambda| 1 + G_0^+ T^+ |\lambda\rangle}\right] \tag{1}$$

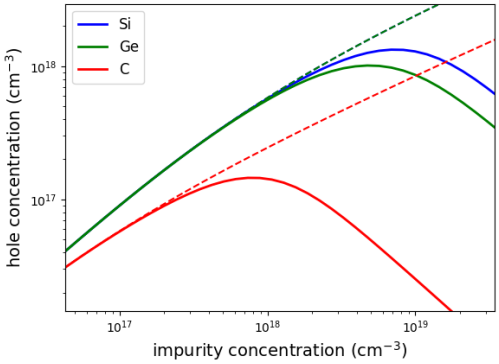
which stems from the Dyson equation $V = G_0^{-1} - G^{-1}$ where G is the Green's function for the defective system. The T - matrix is defined in the main text and Ω_λ are the renormalised frequencies. We assume that Ω_λ^2 scales linearly with the impurity concentration, in line with the dilute defect approximation adopted to compute the phonon-defect scattering rates. We evaluate the quantity $(\Omega_\lambda - \omega_\lambda) \cdot 100 \cdot \omega_\lambda^{-1}$, namely the percentage of how frequencies are shifted in virtue of doping, in Fig. Supplementary Figure 3 and in the case of of neutral C_{As} and Ge_B at the concentration of $4.0 \cdot 10^{21}$ cm^{-3}, with the latter impurities presenting the strongest mass and bond perturbation. It is found that even at such large concentration the shift amounts to less than 1% of the frequencies and can be safely neglected in our conductivity calculations.

II. SUPPLEMENTARY FIGURES

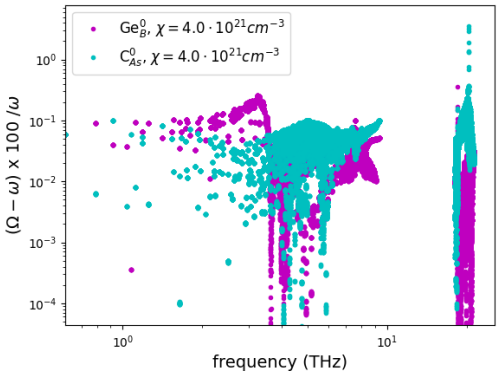
Supplementary Figure 4-Supplementary Figure 9 show the phonon-defect scattering rates (concentration $3.26 \cdot 10^{18}$ cm^{-3}) and the thermal conductivity at 300 K for C, Si and Ge-doped BAs (either acceptors and donors). We see that in the Ge_{As}, Si_B and C_B cases the pure mass perturbation strongly underestimates the reduction in thermal conductivity, while this does not happen for Ge_B, Si_{As} and C_{As}, where the mass variance dominates the spectrum in the $4-8$ THz frequency range. For Ge_B, C_{As} and Si_B the bond perturbation is much larger than in the remaining three defects, although the also large mass perturbation makes it more difficult to distinguish between charged and neutral states, in contrast with the case of Ge_{As} and C_B. Finally, the Si_{As} defect is virtually a mass perturbation-only impurity, due to its large mass variance and very weak bond perturbation.



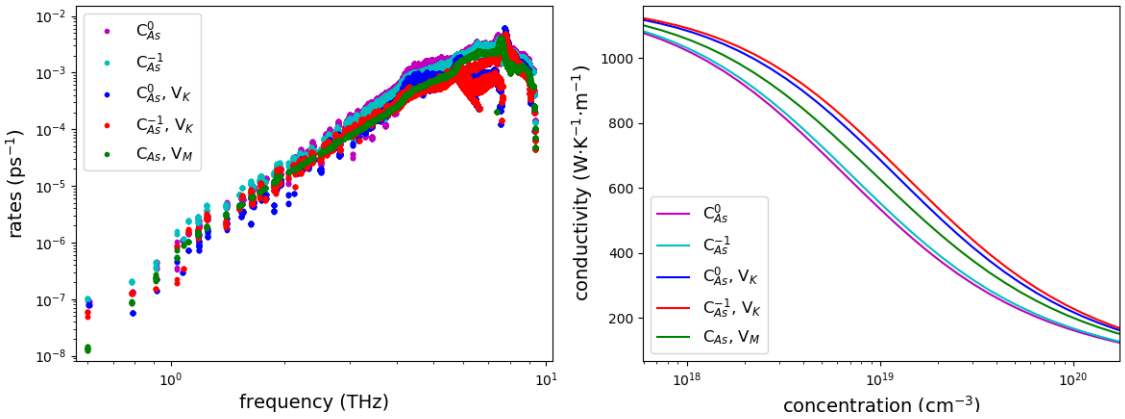
Supplementary Figure 1: Phonon-impurity scattering rates in BAs including only the bond distortions to isolate differences between neutral and charged dopants. Red (blue) points are for charged (neutral) impurities. Dashed vertical lines at 4 THz and 8 THz identify the main frequency region where phonons contribute to the thermal conductivity of pristine BAs. Impurity density is $3.26 \cdot 10^{18}$ cm^{-3}.



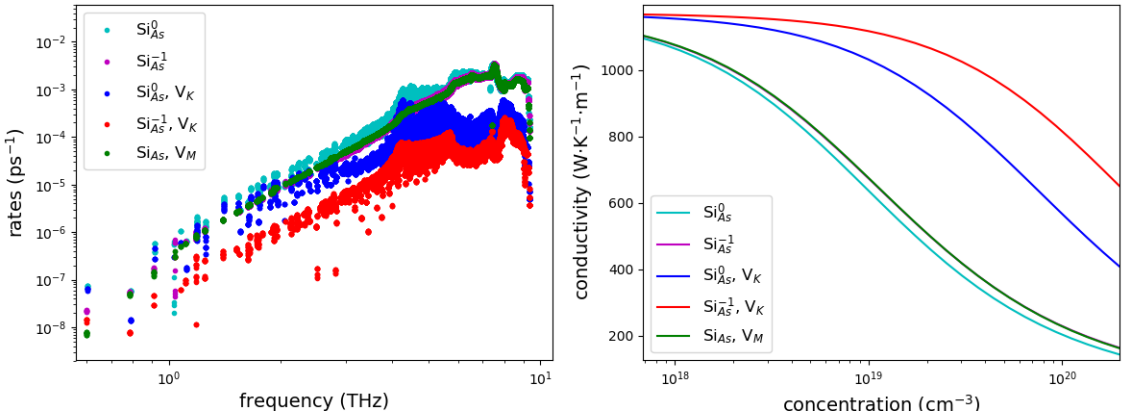
Supplementary Figure 2: Hole concentration in As-rich conditions for Si, Ge and C impurities. Continuous (dashed) lines include (neglect) the presence of donor compensation effects.



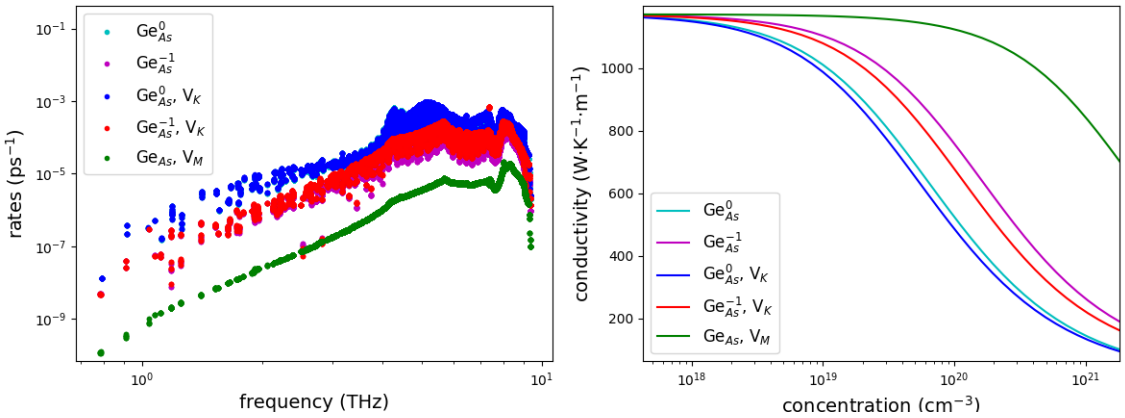
Supplementary Figure 3: Frequency shifts normalised by the pristine BAs phonon frequencies and multiplied by a factor 100 for a concentration of $4.0 \cdot 10^{21}$ cm^{-3} in the case of neutral $\mathrm{C_{As}}$ and $\mathrm{Ge_B}$.



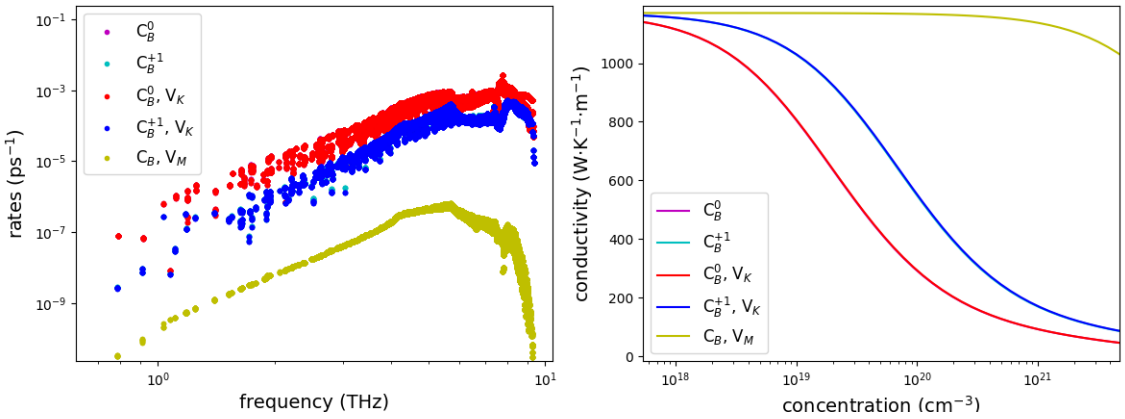
Supplementary Figure 4: C_{As} doped



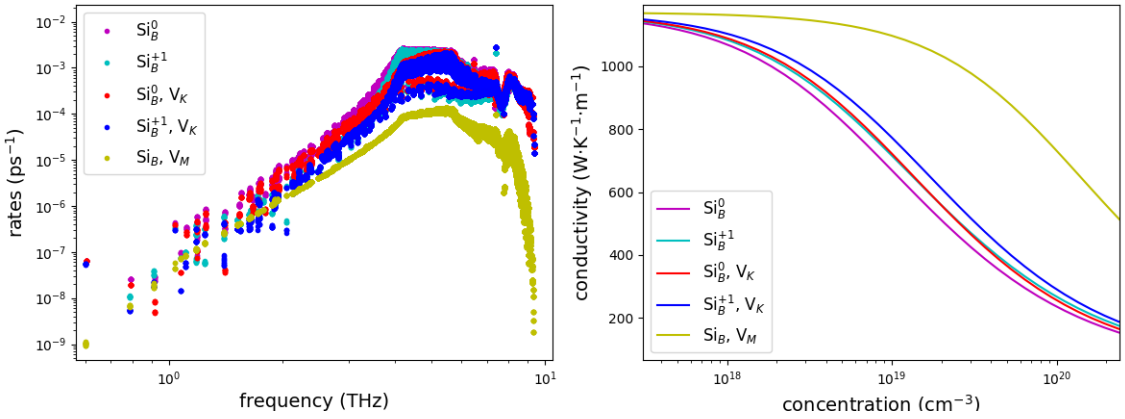
Supplementary Figure 5: Si_{As} doped



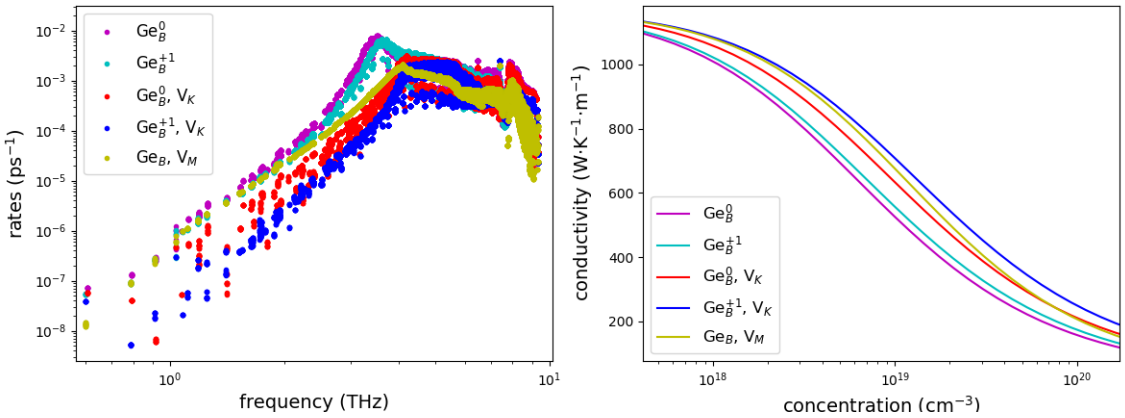
Supplementary Figure 6: Ge_{As} doped



Supplementary Figure 7: C_B doped



Supplementary Figure 8: Si_B doped



Supplementary Figure 9: Ge_B doped

Supplementary References

[1] D. Walton, *Phonon-Defect Interaction* (Springer US, Boston, MA, 1975), pp. 393–440, ISBN 978-1-4684-0904-8.