The intrinsic thermal conductivity of SnSe

ARISING FROM L.-D. Zhao *et al.* *Nature* **508,** 373–377 (2014); doi:10.1038/nature13184

Several groups have been unable to reproduce the record high thermoelectric figure of merit ZT of SnSe reported in ref. 1. Zhao *et al.*[1] measured an ultralow thermal conductivity ($<0.4\,W\,m^{-1}\,K^{-1}$ at 923 K) and consequently record high values of $ZT \approx 2.6 \pm 0.3$ and $ZT \approx 2.3 \pm 0.3$ at 923 K along the b and c directions, respectively, in their single-crystalline SnSe. However, after careful analysis of the data of ref. 1, we deduce that their samples are not fully dense and thus not truly single crystalline, implying that their reported thermal conductivities are not intrinsic to SnSe. This warrants further investigation into intrinsic thermal transport in SnSe single crystals and its use as a thermoelectric material. There is a Reply to this Comment by Zhao, L.-D. *et al.* *Nature* **539,** http://dx.doi.org/10.1038/nature19833 (2016).

In ref. 1, the total thermal conductivity κ of single-crystalline SnSe was calculated using the relation $\kappa = DC_p\rho$, where D is the thermal diffusivity, C_p is the specific heat capacity at constant pressure, and ρ is the density. Although the authors did not list the density of their SnSe crystals, they did provide the diffusivity, specific heat and total thermal conductivity data along the three major crystallographic directions (source data for figure 2d, and extended data figure 6a and b, of ref. 1). We extracted the ρ value for their crystals using the above relation, and found their single-crystalline SnSe samples to be of much lower density (around $5.43\,g\,cm^{-3}$) when compared to the theoretical density ρ_{th} reported in the literature (Table 1). In their Reply to this Brief Communication Arising, Zhao *et al.* confirmed that the experimentally measured density of their samples was indeed lower than ρ_{th}. The ρ value of single-crystalline SnSe estimated from the powder X-ray diffraction studies were in the range 6.13–$6.18\,g\,cm^{-3}$ (Joint Committee on Powder Diffraction Standards (JCPDS) card numbers 01-089-232, 01-089-233 and 01-089-235)[2], while neutron diffraction studies[3] reported a ρ value of about $6.18\,g\,cm^{-3}$ (JCPDS card number 01-071-3877). In addition, electron diffraction studies reported a ρ value of $6.07\,g\,cm^{-3}$ (JCPDS card number 01-075-2123)[4]. In other words, the ρ value for the SnSe samples used in ref. 1 was 88% to 90% of the theoretical density ρ_{th}.

Although the exact cause of the low ρ value in their SnSe samples is beyond our conjecture, in Supplementary Table 1 we compare the reported density and the thermal conductivity values given by several groups for SnSe at 300 K and 750 K, measured along different pressing directions or crystallographic axes. As can be deduced from Supplementary Table 1 and the corresponding scatter plot (Fig. 1), the κ values and the corresponding densities of fully dense single and polycrystalline SnSe reported by different groups are consistently higher than those reported in ref. 1. In the case of polycrystalline SnSe, additional phonon scattering mechanisms are present, which should lead to even lower lattice thermal conductivity κ_L ($\approx\kappa$) compared to the corresponding thermal conductivity of single-crystalline SnSe. Although Zhao *et al.*, in their Reply to this Brief Communication Arising, suggested the formation of SnO_2 as a plausible cause for the higher thermal conductivity in polycrystalline SnSe, it must be noted that SnSe is not highly sensitive to air at ambient temperature[5].

Table 1 | Room-temperature characteristics of the SnSe samples of ref. 1

At about 300 K	*a* axis	*b* axis	*c* axis
Thermal conductivity, κ ($W\,m^{-1}\,K^{-1}$)	0.46525	0.70014	0.67560
Diffusivity, D ($mm^2\,s^{-1}$)	0.33983	0.51139	0.49347
Specific heat, C_p ($J\,g^{-1}\,K^{-1}$)	0.252	0.252	0.252
Density, ρ ($g\,cm^{-3}$)	5.43	5.43	5.43

The densities of the samples of ref. 1 were deduced from the relation $\kappa = DC_p\rho$.

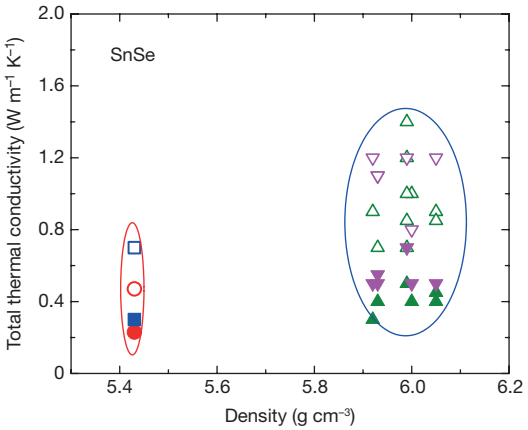

Figure 1 | A scatter plot of thermal conductivity versus density of single and polycrystalline SnSe. The values are taken along different crystallographic axes and along parallel or perpendicular pressing directions, at 300 K and about 760 K, derived from the peer-reviewed literature cited in Supplementary Table 1. The open and solid symbols represent κ at 300 K and 760 K, respectively. The κ values of single-crystalline SnSe along the a axis are represented by red circles and along the b and c axes are represented by blue squares. The κ values of polycrystalline SnSe along the parallel and perpendicular pressing directions are represented by green triangles and violet inverted triangles, respectively. The red ellipse encompasses data from ref. 1 and data reported by other groups[6–21] lie within the blue ellipse. A detailed list of all the data points is available in Supplementary Table 1.

It should also be noted that Zhao *et al.*[1] suggested the presence of "plenty of vacancies and interstitials" in their samples. Some defects are entropically present in single crystals, but we doubt that the vacancies and interstitials can account for the observed 11%–12% deficiency in density at room temperature. It is well known that porosity significantly reduces the thermal transport, which emphasizes the importance of reporting packing density values in future publications to validate the intrinsic transport properties. In other words, true thermal conductivity cannot be obtained by simple normalization, because thermal diffusivity and density are interdependent quantities. Here, we are not expressing concerns about the measurement techniques or the self-consistency of measurements by Zhao *et al.*[1] but about the intrinsic nature of their SnSe single crystals.

Thermoelectricians have long aimed to optimize ZT by reducing κ, and ref. 1 reported exceptionally low thermal conductivity. Thus, the sole aim of this Comment is to correct the scientific record by stating that the ultralow κ value reported in ref. 1 is not intrinsic to fully dense single-crystalline SnSe. A single crystal, by definition, must have an experimentally measured density that is close to 100% of the theoretical density. Thus, the SnSe samples of ref. 1 cannot be classified as single crystalline and the thermal conductivity and figure of merit values for SnSe presented in ref. 1 are not intrinsic to single-crystalline SnSe.

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Received 17 January; accepted 31 August 2016.

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Supplementary Information is available in the online version of the paper.

Author Contributions P.-C.W. and Y.Y.C. contributed towards the synthesis of fully dense SnSe single crystals and the thermoelectric measurements, which were verified by S.B., J.H., R.P., A.M.R. and S.N. This combined study helped us to determine that packing density has a substantial effect on the figure of merit of SnSe.

Competing Financial Interests Declared none.

doi:10.1038/nature19832

Zhao *et al.* reply

REPLYING TO P.-C. Wei *et al. Nature* **539,** http://dx.doi.org/10.1038/nature19832 (2016)

In the accompanying Comment, Wei *et al.*[1] point out that the sample density used to obtain the thermal conductivity value of SnSe crystals is about 10% lower than the theoretical value ρ_{th} and as a result the thermal conductivity is underestimated by about 10%. The data published in ref. 2 are not based on a single measurement or on a single specimen. In the supplementary information of ref. 2 we reported measurements for at least seven crystals with good reproducibility. The material is not a conventional crystal and has several unusual and confusing features, such as the crystallographic phase transition (causing numerous microcracks) and a tendency to oxidation[3–6]. The SnSe crystal also has strong anisotropy and weak mechanical properties, leading to facile cleavage so that the crystal can easily be damaged during cutting and handling. In addition, challenging measurements of this type (that is, thermoelectric measurements on cut single crystals) can show a statistical spread and the error in the measurement of thermal conductivity is typically between 15% and 20% (ref. 7).

The sample density we reported is the value that we measured. Differences between our value and the value(s) measured by others could be caused by differences in sample characteristics arising from preparation methods and handling, or measurement errors. Regardless of whether the density of the SnSe crystal is 6.0 g cm^{-3} or 5.5 g cm^{-3}, the lattice thermal conductivity is ultralow, in the ranges 0.6–0.8 W mK^{-1} at room temperature and 0.3–0.4 W mK^{-1} at 800 K. In hole-doped SnSe crystals[7,8], where a different experimental density was measured (closer to the theoretical 6.0 g cm^{-3}), the lattice thermal conductivity is in agreement with the value we report in ref. 2. If the experimental density is adjusted 10% upwards to be closer to the theoretical value of 6.1 g cm^{-3}, the thermal conductivity is still ultralow. Therefore, sample density does not greatly affect the ultralow value of the lattice thermal conductivity. Whether the thermal conductivity is intrinsic to SnSe is not yet clear, but some explanations have recently been proposed[3,5].

The sample prepared by Wei *et al.* and described in their Comment was grown under different conditions, the details of which are not known to us. Must an 'intrinsic' value refer to a material with exactly stoichiometric composition, vacancy-free, dislocation-free, strain-free, fully dense, and with the number of excited electrons equal to the number of holes? Or could an 'intrinsic' value refer to the most stable state of a material for a given set of experimental growth conditions? The SnSe sample of a recent publication has an Sn vacancy rate of several per cent[9], which is consistent with our observations of a large off-stoichiometry of Sn:Se (0.835:1) in SnSe crystals prepared using the Bridgman method; however, no off-stoichiometry was observed in SnSe crystals synthesized using a vapour-transfer method. Thus we consider it unfair to conclude, as do Wei *et al.* in their Comment, that our value for lattice thermal conductivity is not 'intrinsic' to SnSe, on the basis of the sample density only.

The true measure of the thermal conductivity lies in the thermal diffusivity data, which show very low values. The question of

interest concerning SnSe is whether or not it has an ultralow thermal conductivity, and most reported values for samples of SnSe suggest that it does[2,3,10–14]. The reported values have a spread[7], but this is not surprising given (1) the challenges in measuring materials with ultralow thermal conductivity, (2) variations from sample to sample with respect to defects, phase-transition cracks, and so on, and (3) several variations in the synthesis of the material[5]. Of all reports on polycrystalline SnSe samples[2,3,7,8,10–36] at room temperature, 55% report higher thermal conductivity than in the single crystal[2], 25% report similar values, and 20% report a lower thermal conductivity. At 800 K, about 15% report higher thermal conductivity than in the single crystal[2], 80% report similar values, and 5% report a lower thermal conductivity.

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doi:10.1038/nature19833