Electronic Supplementary Information

Grain boundary dominated charge transport in Mg_3Sb_2-based compounds

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I. FAILURE OF MATTHIESSEN'S RULE IN DESCRIBING THE TEMPERATURE EXPONENT CROSSOVER

Mixed scattering mechanisms in charge transport is typically modeled using Matthiessen's rule on the relaxation time (*i.e.* $\tau^{-1} = \sum \tau_i^{-1}$), which is an approach that effectively constructs a homogeneous system. Here we show that, when two scattering mechanisms with different temperature dependencies are combined with Matthiessen's rule, it is *not* possible for the system to show a sharp transition from one to another unless at low temperatures.

Consider the mixed scattering case with both acoustic-phonon scattering (APS) and ionized-impurity scattering (IIS). The total scattering rate with Matthiessen's rule is:

$$\frac{1}{\tau} = \frac{1}{\tau_{\mathrm{APS}}} + \frac{1}{\tau_{\mathrm{IIS}}}. \tag{S1}$$

Here, $\tau_{\mathrm{APS}} \propto T^{-3/2}$ and $\tau_{\mathrm{IIS}} \propto T^{3/2}$. For simplicity, we assume the non-degenerate limit where conductivity is described with a constant drift mobility with respect to E_{F} (the final conclusion drawn here remains similar in the general case). Then, drift mobility μ_{d} scales to the power of temperature with an exponent $(d\log\mu_{\mathrm{d}}/d\log T)$ corresponding to $-3/2$ and $3/2$ for pure APS (high T limit) and IIS (low T limit), respectively.

At a cross over temperature T_{C}, the two scattering mechanisms have comparable scattering rates:

$$\frac{1}{\tau_{\mathrm{APS}}} = \frac{1}{\tau_{\mathrm{IIS}}} \qquad (T = T_{\mathrm{C}}). \tag{S2}$$

Therefore, by combining Eqs.S1-S2 the power exponent of temperature for drift mobility can be expressed in terms of T/T_{C}:

$$\frac{d\log\mu_{\mathrm{d}}}{d\log T} = \frac{d\log\tau}{d\log T} = \frac{3}{2} - \frac{3(T/T_{\mathrm{C}})^3}{1+(T/T_{\mathrm{C}})^3}, \tag{S3}$$

which would be the slope observed in a $\log\mu_{\mathrm{d}} - \log T$ plot. The result is plotted in Fig.S1 which shows a transition from IIS $(-3/2)$ to APS $(3/2)$ with increasing temperature.

To observe a crossover from IIS to APS, T/T_{C} must change from about 0.5 to 2.0, which means that for a $T_{\mathrm{C}} = 500$ K the crossover would have to happen gradually from 250 K to 1000 K rather than drastically. This finding contradicts the sharp crossover experimentally found in Mg_3Sb_2-based compounds.

II. DETERMINING THE FUNCTIONAL FORM OF THE BAND OFFSET

Here we detail how the empirical function used to describe the E_{F} dependency of the band offset was determined. We find the best offset value yielding the least square error in conductivity for each individual sample around a local temperature range and plot it with respect to the Fermi-level of the grain phase $E_{\mathrm{F,G}}$ (Fig.S2). $E_{\mathrm{F,G}}$ was determined using the Seebeck measurements in accordance to Eqs.6-7 and all model parameters were fixed to values listed in Table.1.

The compilation of individually optimized offset values (Fig.S2) indicate that a linear function could capture the overall trend with a minimal number of fitting parameters. We therefore use a function form of Eq.1 with fixed parameters $\Delta E = 60$ meV and $a = 0.3$ for the entire data set considered in this study.

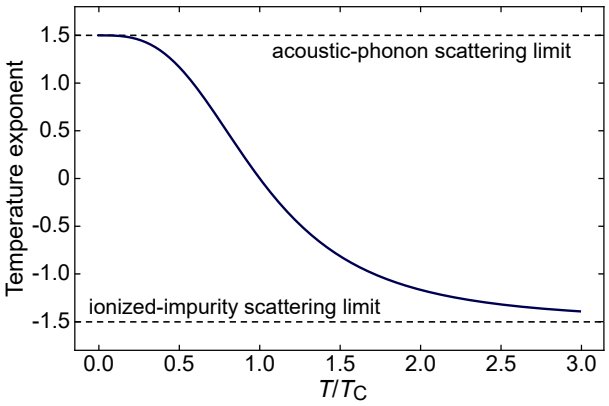

FIG. S1. The slope that would be observed in a $\log \mu_{\mathrm{d}}$-$\log T$ plot as a function of reduced temperature T/T_{C}. Note the APS and IIS signature slopes (3/2 and $-3/2$) at high and low T, respectively.

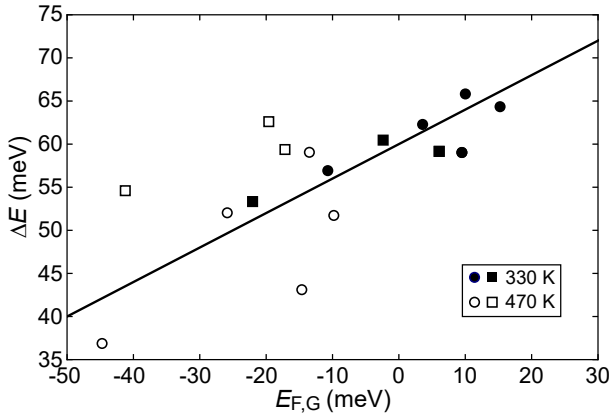

FIG. S2. Band offsets optimized for individual samples and temperatures for the purpose of finding the empirical offset function universal for the entire sample set. Circled data points are from Ref.1; squared points are from Ref.2. The Fermi-levels are measured from the conduction band edge of the neutral grain.

REFERENCES

[1] J. Shuai, J. Mao, S. Song, Q. Zhu, J. Sun, Y. Wang, R. He, J. Zhou, G. Chen, D. J. Singh, and Z. Ren, Energy & Environmental Science **10**, 799 (2017).

[2] H. Tamaki, H. K. Sato, and T. Kanno, Advanced Materials **28**, 10182 (2016).