Experimental report

19/10/2018

Proposal:	**7-01-475**	**Council:**	4/2018

Title: Is AgCrSe2 really a liquid-like thermoelectric?

Research area: Materials

This proposal is a new proposal

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Samples: AgCrSe2

Instrument	Requested days	Allocated days	From	To
THALES	5	5	12/09/2018	17/09/2018

Abstract:

The development of next generation thermoelectrics requires materials with extremely low thermal conductivities. Recently much attention has focussed on the so-called Phonon-Liquid Electron-Crystal concept where superionic diffusion is supposed to prevent transverse acoustic phonons from propagating, leading to ultra-low thermal conductivity. It has been suggested that AgCrSe2 is a PLEC material on the basis on unpolarised neutron-TOF data. However, there is a strong possibility that scattering attributed to diffusion is, in fact, magnetic in origin. This proposal will probe the origin of this scattering and determine if AgCrSe2 is really a liquid-like thermoelectric.

Experimental report 7-01-475: Is $AgCrSe_2$ really a liquid-like thermoelectric?

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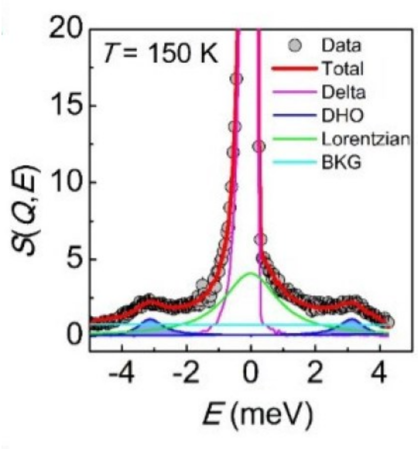
The aim of this experiment was to test the idea that the superionic thermoelectric $AgCrSe_2$ enters a "liquid-like" phase above the superionic transition (450 K). This is characterised by a loss of the transverse acoustic phonons above the transition temperature due to a diffusive process with residence times shorter than the typical phonon period. In an inelastic neutron experiment this would be evidenced by a quasi-elastic signal in the spin-incoherent channel, where the half-width approaches the phonon energy.

Unpolarised measurements on $AgCrSe_2$ have suggested that this criterion is met and that there is even significant QENS at temperatures far below the superionic transition [1]. We have hypothesized that the signal attributed to QENS is magnetism and that in fact the material is not a "phonon-liquid".

ThALES was set up in polarised mode with the Helmholtz coils and doubly-focussing Heusler monochromator and analyser. Permanent magnet guide fields were used to transport the polarisation to and from the Helmholtz coils. The non-spin-flip cross sections were each measured for approx. 1 minute per point (90,000 counts m1), the spin flip *y* and *z* cross sections were counted 3 times as long and the spin-flip x was counted 12 times as long giving roughly equal contributions to the errors. Energy scans were performed with a fixed final energy of 8 meV. Datasets were collected at 5 K (in the magnetically ordered regime), 150, 300, 400 K and at 500 K (above the superionic transition) at fixed $Q = 2.16\ \text{Å}^{-1}$. The flipping ratios were approximately 20 for each cross section.

Figure 1 shows the results of (a) multispectral fitting from Ref. [1] and (b) our polarised neutron results. It is clear that the QENS signal is magnetic in origin. There is no quasi-elastic energy broadening of the spin-incoherent scattering. The peak in the nuclear scattering at 3 meV is a transverse acoustic phonon. [In addition, there is a small spurion at 0.5 meV in the nuclear and spin-incoherent channels with no temperature dependence.



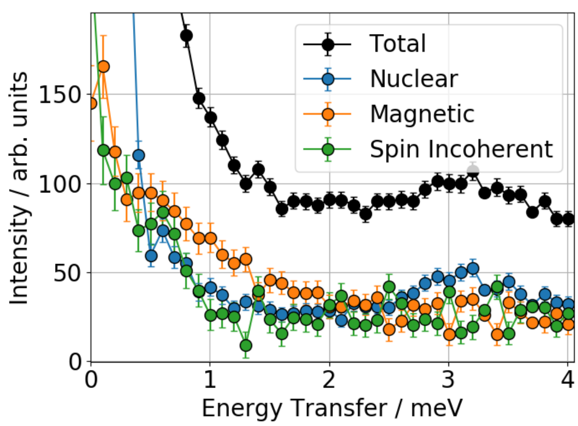


Figure 1: (a) The multi spectral fitting performed in Ref. [1] and (b) our polarised measurement at the same Q at 150 K which enables us to isolate the nuclear, magnetic and spin-incoherent cross sections.

The evolution with temperature shown in figure 2 helps to understand the origins of the scattering. The magnetic scattering continuously broadens as the temperature is increased with no dramatic change above the superionic transition. The spin-incoherent scattering exhibits no detectable quasi-elastic energy broadening, and away from the elastic line gradually increases in intensity as would be expected from the increase in population of the phonon-density of states. The nuclear cross section is very informative. Below the superionic transition the phonon broadens rapidly, consistent with very strong anharmonic phonon scattering. The nuclear scattering changes dramatically in the superionic phase with the sudden arrival of QENS at 500 K.

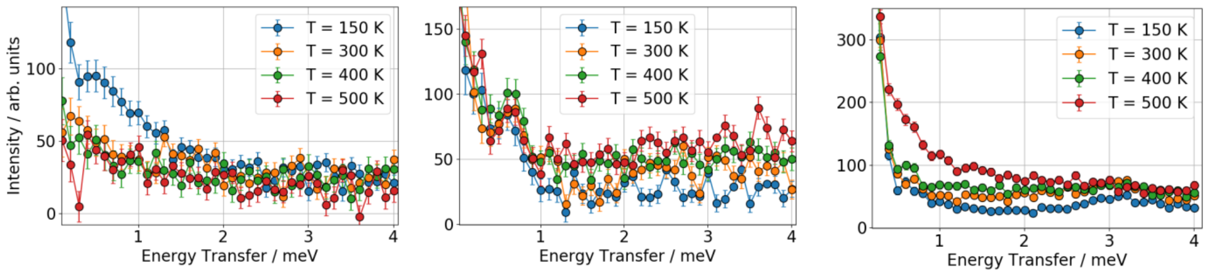


Figure 2: (a) The magnetic (b) the spin-incoherent and (c) the nuclear cross section showing the phonon at 3 meV and the coherent QENS in the superionic phase.

The spin-incoherent channel gives information on the self-correlation function, and the fact that in this case the QENS is not incoherent tells us that it is not due to Ag diffusion. Instead, the coherent cross section tells us about correlations between different sites. Above the superionic transition the Ag sits fractionally on an interstitial site [1] and this gives rise to coherent diffuse scattering. Similar behaviour has been seen in the superionic fluorites where the anion moves to an interstitial site creating a Frenkel defect. Such dynamic defects clusters, give rise to coherent diffuse scattering with an energy broadening which can be interpreted in terms of the lifetime of the correlations associated with the diffusing ion [2].

Hence, we are able to rule out the Phonon-Liquid Electron-Crystal model for $AgCrSe_2$. Instead we find clear evidence of an increase in dynamic defects in the superionic phase that can scatter phonons and may well be responsible for the small drop in lattice thermal conductivity above the superionic transition.

References

1) B. Li *et. al., Nature Materials,* **17**, 226-230 (2018).

2) M. T. Hutchings *et. al., Journal of Physics C: Solid State Physics,* **17,** 3903 (1984)