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Structure-transformation-induced abnormal thermoelectric properties in semiconductor copper selenide

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ABSTRACT

Thermoelectric effects and related technologies have attracted a great interest due to world-wide energy harvesting. Thermoelectricity has usually been considered in the context of stable material phases. Here we report that the fluctuation of structures during the second-order phase transition in Cu_2Se semiconductor breaks the conventional trends of thermoelectric transports in normal phases, leading to a critically phase-transition-enhanced thermoelectric figure of merit zT above unity at 400 K, a three times larger value than for the normal phases. Dynamic structural transformations introduce intensive fluctuations and extreme complexity, which enhance carrier entropy and thus the thermopower, and strongly scatter carriers and phonons as well to make their transports behave critically.

1. Introduction

Thermoelectricity is a direct means of converting heat into electricity and vice versa [1,2]. It has a potential impact on efficient harvesting and conversion of waste heat into electricity as well as serving as a fully solid-state heat pump. The energy conversion efficiency of thermoelectric (TE) technology is mainly limited by materials' performance described by the dimensionless TE figure of merit zT ($zT=S^2\sigma T/\kappa$). It is composed of absolute temperature T and three intrinsic physical quantities: thermopower S, electrical (σ) and thermal (κ) conductivities. Due to the mutual interdependence of transport parameters, it is a challenging task to optimize the structure in order to obtain as high a zT as possible. The three intrinsic quantities strongly intercorrelate with each other, resulting in the fact that the reported TE performance shows the physical-law-confined gradual temperature dependence. In order to achieve high TE performance, the general approach is to make the static structures of a material as complex as possible to compromise the transports of carriers and phonons. This approach has been successfully applied in many TE materials to effectively improve TE performance from single phases to hybrid materials such as nano-wires [3,4], thin films [5], superlattices [6], or nano-structured materials or composites [7,8]. Here, we show that the structure fluctuation during second-order phase transition in semiconductor Cu_2Se could break the conventional trends of TE transports in normal material phases, leading to a critically phase-transition-enhanced thermopower and sharply-improved zT by a factor of three times within a small temperature range of 40 K.

2. Results and discussion

Structural phase transformations are common occurrences observed in many of the solid-state materials with intrinsically complex structures. One of such is Cu_2Se [9–11] which at temperatures above 400 K occurs in the cubic β phase of high symmetry while at lower temperatures it is in the α phase of low symmetry. It undergoes a structural phase transformation at the transition temperature T_c about 400 K [9]. Above T_c, Cu_2Se has a cubic anti-fluorite structure in which the selenium atoms occupy a face centered cubic (fcc) lattice with the copper ions distributing disorderly on the trigonal and tetragonal interstitial sites. Below T_c, Cu_2Se transforms to the α phase, and the cubic symmetry of the β phase is lowered by the structural distortion [9].

By focusing on the Cu_2Se sample with a slight Cu deficiency, measured transport properties are found to depict surprising

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large TE effects in a rather broad phase transformation domain occurring in temperature range of 350–400 K. Within the α and β phases, the temperature-dependent transport properties change continuously and slowly, but they are all sharply modified when the temperature reaches the onset temperature T_0, which separates the measured thermopower from the linear extrapolation of α-Cu_2Se shown in Fig. 3a. The S rises sharply as T_c is approached, enhanced by a factor of at least two before it falls to its normal value above 400 K (Fig. 1(a)). Values of σ and D decrease about four times in magnitude when the critical point is approached and then jump sharply back to the normal value on the other side of the transition in the β phase when temperature is >400 K. We have also cycled measurement temperature (both heating and cooling cycles) of our samples to test the data reproducibility and found that the data are entirely consistent, indicating the intrinsic behavior of TE transports. Based on the measured TE transport, the calculated figure of merit zT is critically enhanced near T_c, and reaches values above unity, a factor of three times larger value than for the normal α or β phases of Cu_2Se.

The abnormal thermoelectric properties observed in transport properties are the consequence of the phase transition in Cu_2Se, as demonstrated by the Differential Scanning Calorimetry (DSC) measurement (Fig. 2(a)) and High-temperature X-Ray Diffraction (HTXRD). DSC reveals a critical increase in the specific heat and confirms T_c around 400 K. The onset temperature of the phase transition is estimated to be around 350–360 K according to the baseline shown in Fig. 2(a). HTXRD shows that room temperature α phase gradually transforms to the cubic β phase upon heating the sample. The conversion rate increases as temperature approaches T_c; at this temperature the entire α phase is completely transformed to the β phase (~400 K), consistent with the DSC measurement. The coalescence of split peaks around

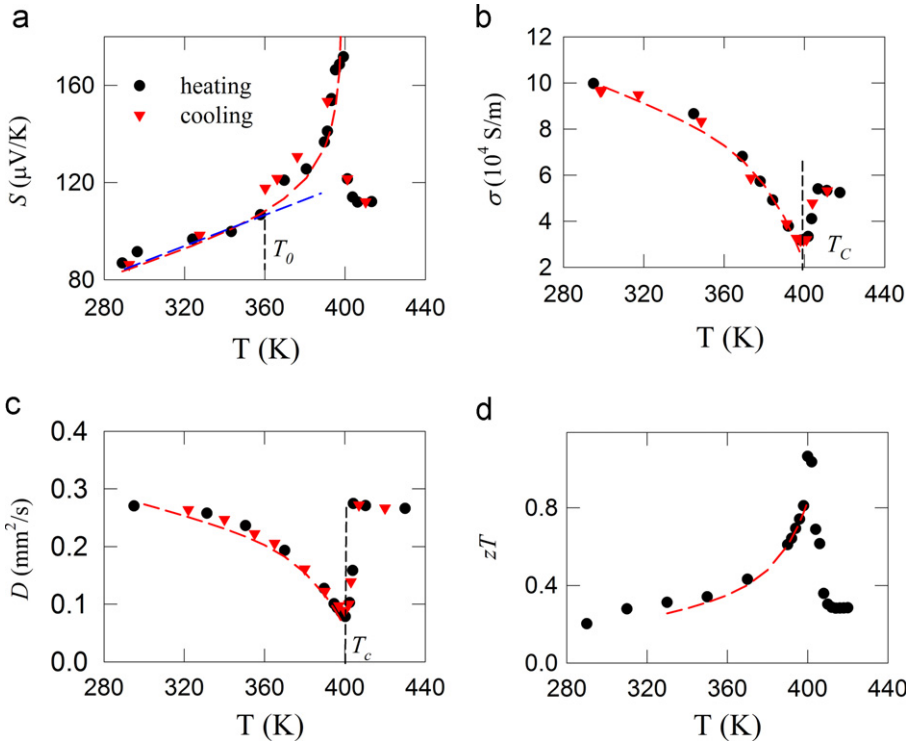

Fig. 1. Thermoelectric properties of Cu_2Se between 300 K and 440 K. (a) Temperature dependence of thermopower S, (b) electrical conductivity σ (c) thermal diffusivity D and (d) the dimensionless figure of merit zT. The red lines in (a)–(c) are the fitted data using Eqs. (2) and (3). The blue dashed line in (a) is a linear extrapolation for the low-temperature thermopower data of α-Cu_2Se. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

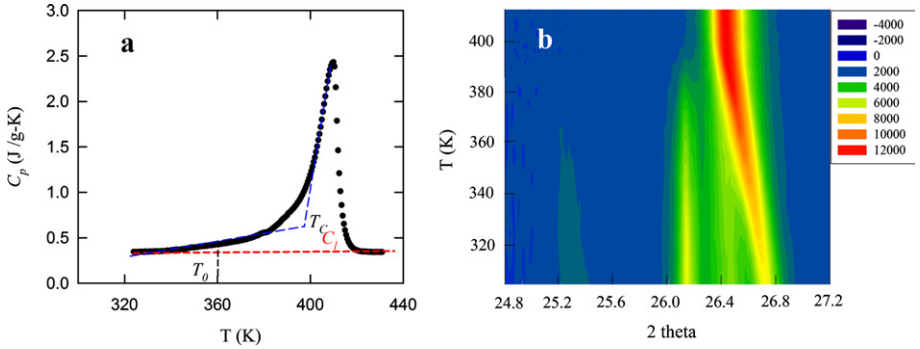

Fig. 2. Differential Scanning Calorimetry (DSC) and High-temperature X-Ray Diffraction (HTXRD) measurements for Cu_2Se. (a) Measured specific heat (C_p). The phase transition temperature is around 400 K (T_c). C_L is the contribution from lattice vibrations (Dulong–Petit value). The starting onset temperature (T_0) of the phase transition is estimated to be between 350 and 360 K. (b) HTXRD data collected on heating of Cu_2Se from 300 K (bottom) to 410 K (top), showing the coalescence of the split peaks around 26.4–26.7° and the disappearance of the extra peaks around 26.15° as the lower-symmetry α phase transforms to the higher-symmetry cubic β phase.