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Viewpoint Paper

Search for non-equilibrium thermoelectrics

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ABSTRACT

Since thermoelectrics is an energy-conversion technology from heat flow to electrical flow, or vice versa, it is essentially a non-equilibrium phenomenon in the sense that energy and particle flows are involved. We have recently focused on this feature in order to overcome theoretical predictions of the upper limit of the conversion efficiency in thermal equilibrium conditions. One trial is the thermoelectric phenomena in the range of non-ohmic conduction. The second approach is the thermoelectric phenomena shown by the photo-doped carriers.

1. Introduction

Thermoelectric phenomena in solids have been extensively investigated from the point of both scientific and technological interests [1]. They are tightly related to thermodynamic properties of conducting electrons, known as the transport entropy in solids. At the same time, they offer an efficient way to directly convert heat into electric energy, or vice versa, which enables us to recover electric power from waste heat and to refrigerate objects electronically. Such energy conversion technology is called *thermoelectrics* [2,3]. For the last decade, we have proposed and investigated oxide thermoelectrics: thermoelectric energy conversion using oxide materials [4].

Materials' performance for thermoelectric energy conversion is characterized by the figure of merit $Z = S^2/\rho\kappa$, where S the Seebeck coefficient, ρ the resistivity, and κ is the thermal conductivity. When the temperature dependence of S, ρ and κ can be neglected, the energy conversion efficiency is determined by the dimensionless figure of merit ZT, where T is the absolute temperature. Accordingly, a good thermoelectric material requires low conductivity, large Seebeck coefficient, and low thermal conductivity simultaneously. Since the three parameters are related to one another, a large ZT value is difficult to find in existing materials, and $ZT = 1$ is a practical goal for applications. In fact, reliable calculations of materials parameters do not give $ZT > 3$.

We should emphasize that such theoretical predictions are based on equilibrium states, and there remains a possibility that the thermoelectric performance may go beyond theoretical limitations when the system is out of equilibrium. For example, Casati et al. [5] theoretically proposed a model ballistic system, in which the ZT value exceeds ten against properly chosen parameters. In this article, we show our preliminary results for two types of non-equilibrium thermoelectrics. One is thermoelectric properties in large current density, and the other is thermoelectrics using photo-doped carriers.

2. Non-equilibrium states

The word of non-equilibrium covers a wide range of states, because it means any states that are *not* in thermal equilibrium. In equilibrium states, macroscopic thermodynamic variables are uniquely determined by a small number of macroscopic variables, the relationship of which is given by thermodynamics. Even when the system is slightly out of equilibrium, the response of the system can be quantitatively predicted from the original equilibrium state through the fluctuation–dissipation theorem. Thus the non-equilibrium states we discuss in this article are those far from thermal equilibrium, where conventional thermodynamics and statistical physics are not justified to apply.

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Transient phenomena at short time scale are most remarkable non-equilibrium states [6]. Thanks to recent development in pulsed laser technique, we can observe response of a system with a time resolution ranging from femto- to pico-seconds. Since the electric field intensity of the incident laser pulse can be very large, one can observe various truly non-equilibrium phenomena such as photo-induced phase transitions [7]. These are quite interesting from the viewpoint of fundamental science, but the time scale is too short for thermoelectrics. In fact, after a "long" time (say, 1 μs), absorbed photon energies are dissipated into heat to warm up the sample.

Much slower transient phenomena can effectively work in electronic refrigeration. Miner et al. [9] have proposed that the temperature drop of a Peltier device can be enhanced by a factor of two by applying a short current pulse of 0.1–0.5 ms in addition to a direct current. The mechanism is that at the cold end, the Peltier refrigeration occurs instantaneously, but the Joule heat generated in the center of the device reaches late. Thronhauser et al. [8] have shown a simulation for the transient cooling as shown in Figure 1. A direct current is applied in the device in advance, and the temperature at the cold end is initially kept at 220 K. Then a current pulse shown by the dashed curve is additionally applied, and the calculated temperature is plotted by the solid curve. The temperature reaches down to 182 K at 500 μs, which means ΔT increases from 80 to 118 K. Since ΔT is directly proportional to ZT, the result in Figure 1 indicates that an effective ZT value increases by 50%. After the pulse is turned off, the temperature goes up to 240 K owing to the Joule heat arriving late at the cold end. Later Yan and Malen [10] has experimentally observed that the efficiency in such a transient mode can be enhanced by a factor of five.

A second example is a non-dissipative transport such as ballistic transport in nano-structured materials. Humphrey and Linke [11] have theoretically proposed a reversible thermoelectric nano-device, and have shown that the efficiency equals the Carnot efficiency. Unfortunately, this device works only in open circuit conditions, and the power (work per unit time) is zero. Wu et al. [12] have observed anomalous enhancement of the power factor S^2/ρ in an InAs nanowire device, which is ascribed to the interference of the propagating electrons. Another type of non-dissipative transport is the thermionic emission, a tunneling phenomenon of a thermally excited electron. Mahan and Woods [13] have proposed a thermionic refrigerator using a multilayer film, and Shakouri and his coworkers [14,15] have made thermionic devices using semiconductor superlattices.

The non-equilibrium state we have studied thus far is a non-equilibrium steady state (NESS)—yet another non-equilibrium state, where the system is in a steady state with constant flows of particle and energy [16]. NESS has been regarded as a most simplified model for biological systems in the sense that it mimics homeostasis with exchanging substances and/or energies against the surroundings [17]. In the next sections, we will show anomalous thermoelectric properties in NESS.

3. Thermoelectrics in high current density

Non-ohmic conduction is a typical example for NESS, and among such systems we have focused on nonlinear conduction phenomena in strongly correlated electrons. As is generally agreed, strong correlation is a fertile source of electronic phase transitions such as high-temperature superconductivity in copper oxides, colossal magnetoresistance in manganese oxides, and multipole ordered states in heavy fermion intermetallics. Since some of such ordered states are susceptible to external impetus, we have searched for an ordered state susceptible to external electric field.

Eventually we discovered giant nonlinear conduction in an organic salt θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ [18], as shown in Figure 2, and ascribed this to the suppression of the charge ordering by external current [19]. The charge order is one of the ordered states in strongly correlated electrons, in which conduction electrons form a lattice in order to minimize the Coulomb repulsion [20]. Since external current introduces electrons and holes to the system, it adversely affects the insulating nature of charge ordering. Ajisaka et al. [21] theoretically calculated this situation, and found that the external current reduces the charge-order gap. Other theoretical approaches have been reported to explain the nonlinear conduction of this compound [22,23]. We further found that this organic salt exhibited a current oscillation with a dc voltage bias [24]. Such an oscillation is an intrinsically

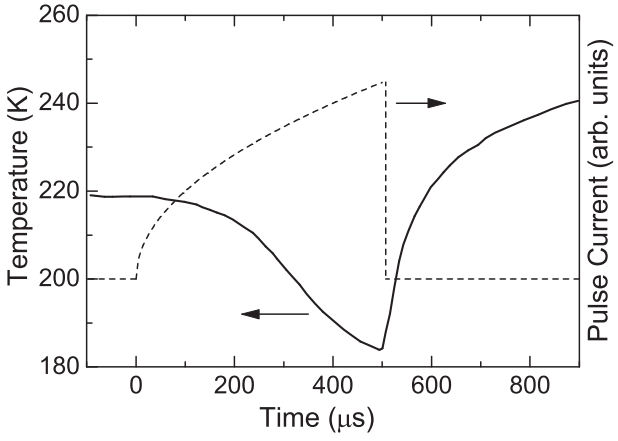

Figure 1. Calculated transient thermoelectric response [8]. A direct current is applied to a Peltier device, and the temperature at the cold end is kept at 220 K for $t < 0$. Then a current pulse shown by the dashed curve is added, which significantly decreases the cold-end temperature down to 180 K at 500 μs.

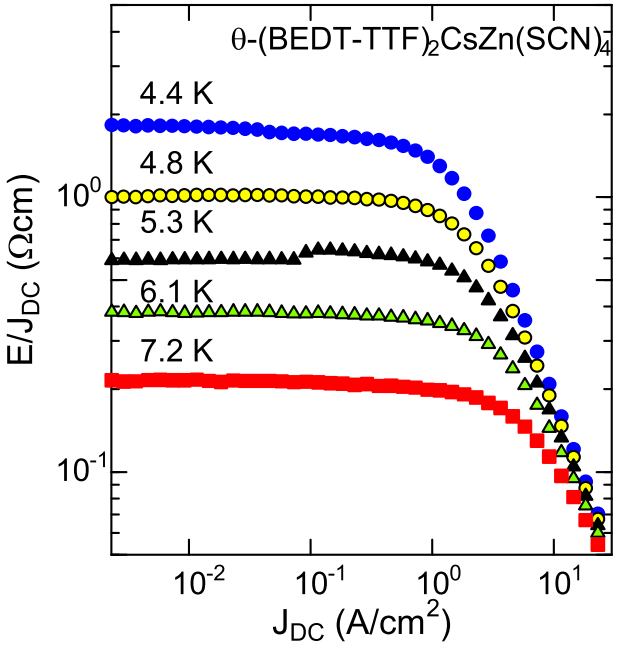

Figure 2. The resistivity of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ plotted as a function of current density.