

Thermoelectric Power of Kondo Insulators

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Abstract

Thermoelectric power (TEP) of the Kondo insulators is investigated theoretically within the framework of the dynamical mean field theory. It is found that the temperature dependence of the Seebeck coefficient changes from the ordinary behavior $S(T) \propto T^{-1}$ in semiconductors to $S \propto T$ at low temperatures due to the finite imaginary part of the electron self-energy in the Kondo insulators with strong correlation. Realistic models for YbB_{12} and FeSi based on the band calculations are also studied.

Keywords: A. semiconductors, D. transport properties

§1. Introduction

Thermoelectric power (TEP) is currently attracting renewed interest because of the increasing need for a portable refrigerator without use of vapor coolant[1]. Narrow gap semiconductors have been intensively studied so far for such purpose and Bi_2Te_3 and its alloys are found to be the most efficient material (highest figure of merit $Z = S^2/\kappa\rho$, where S , κ and ρ denote, respectively, Seebeck coefficient, the thermal conductivity and the resistivity). It has been known that some alloys with magnetic impurities and the so-called heavy-fermion compounds which include Ce or Yb atoms as constituents also show large TEP ($|S| \lesssim 100\mu\text{V/K}$). This is because of the strong energy-dependence of the carrier relaxation time due to Kondo-type scattering in these materials, and has been studied theoretically by using the non-crossing approximation and the Bethe Ansatz approach.[2, 3, 4] These theories predict the positive (negative) TEP at temperatures lower than the Kondo temperature T_K for Ce (Yb) ions, mostly in agreement with the experiments. The TEP makes a peak around T_K and the absolute value decreases above it. In some of the compounds (e.g. CeCu_2Si_2), however, the TEP changes the sign at low temperatures, which can not be explained by the Kondo or Anderson impurity models. This phenomena is attributed to the effect of magnetic fluctuations, but a detailed study is still necessary.

Recently, however, materials with much higher values of $|S|$ were found in the compounds called Kondo insulators. For example, YbB_{12} , a typical Kondo insulator with the energy gap of the order of 100K, shows $|S|_{\text{max}} \sim 140\mu\text{V/K}$ at around $T = 100\text{K}$ [15], and FeSi, the Kondo insulator of the transition metal element, exhibited $S_{\text{max}} \sim 500\mu\text{V/K}$ at $T = 50\text{K}$ [6]. These materials show large TEP only at rather low temperatures, but it may be advantageous for a refrigerator which works at low T .

It is well known[1] that $S(T) \sim -(k_B/e) (E_{c,v} - \mu)/k_B T$ for semiconductors, where $E_{c,v}$ denotes the gap edge position of the conduction or valence bands and μ the chemical potential. Our first concern in the present study is how this is modified for the Kondo insulators with strong correlation. We study it by using the dynamical mean-field theory (DMFT)[7] for the periodic Anderson model (PAM), and will find that the rise of S in proportion to $(k_B T)^{-1}$ turns into $k_B T$ at low temperatures due to the

finite imaginary part of the electron self-energy. We also study two-band models with the density of states calculated from the APW band calculations and apply them to YbB₁₂ and FeSi. Comparisons with experiments and discussions will be presented in the last section.

§2. Boltzmann equation

Seebeck coefficient S is given by the sum of the electron diffusion and the phonon drag terms. As will be found below, the former is enhanced in most of the strongly correlated materials. Therefore, we focus only on the electron term and call it simply as S . By using the Boltzmann equation, S is given by

$$S(T) = -\frac{1}{eT} \int d\epsilon L(\epsilon)(\epsilon - \mu) \left(-\frac{\partial f}{\partial \epsilon} \right) / \int d\epsilon L(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right), \quad (1)$$

where $L(\epsilon) \equiv \rho_c(\epsilon)v_c(\epsilon)^2\tau_c(\epsilon)$ and $\rho_c(\epsilon)$, $v_c(\epsilon)$ and $\tau_c(\epsilon)$ denote the density of states (DOS), velocity and the relaxation time of conduction electrons, respectively. This formula yields the well-known result $S(T) \sim -(k_B/e) (E_{c,v} - \mu)/k_B T$ for semiconductors. On the other hand, the Peltier coefficient Π is related to S as $\Pi = TS$, hence $\Pi \sim (E_{c,v} - \mu)/e$ remains finite even at low temperature limit. The Peltier coefficient is defined as the heat absorbed or emitted at the junction of two elements when a unit charge flows through it. Therefore, it would turn out that the third law of the thermodynamics is broken if Π remains finite at $T \rightarrow 0$. To avoid this contradiction, one would have to carefully investigate the electron-phonon coupled Boltzmann equation, taking full account of the nonequilibrium state of the phonon system as in [8]. In the present paper, however, we will show below that the many-body effect will resolve this problem through the self-energy which is not included in the Boltzmann approach.

§3. Periodic Anderson model

In DMFT,[7] the TEP is given by the same formula as (1) but with

$$L(\epsilon) = \frac{1}{\pi N} \sum_{\mathbf{k}} v_{c\mathbf{k}}^2 [\text{Im}G_c(\mathbf{k}, \epsilon)]^2, \quad (2)$$

where $G_c(\mathbf{k}, \epsilon)$ and $v_{c\mathbf{k}}$ are the Green's function and the velocity of conduction electrons. The vertex correction drops out in this theory.

Schweitzer and Czycholl[9] applied this scheme to the PAM and calculated the TEP for the metallic cases by using the self-consistent second-order perturbation theory. We here investigate the case of the Kondo insulators.

The Kondo insulators are the band insulators with strong correlation between f (or d in the case of FeSi) electrons.[10] The PAM is the simplest model for them. We use the DMFT scheme mentioned above and calculate the self-energy by the iterative perturbation theory in a modified form (mIPT).[11]

To evaluate eq.(2), however, one has to perform the \mathbf{k} -summation over the Brillouin zone, which requires tedious numerical calculations. When the anisotropy is weak, however, $L(\epsilon)$ can be approximated by $L(\epsilon) \simeq v_F^2 \rho_c(\epsilon) \tau_c(\epsilon)$. Here the velocity is assumed constant and replaced by the Fermi velocity v_F . In the case of the PAM, $\rho_c(\epsilon)$ and $\tau_c(\epsilon)$ are given by

$$\rho_c(\epsilon) = -\frac{1}{\pi N} \text{Im} \sum_k \frac{1}{\epsilon - \epsilon_k - \frac{V^2}{\epsilon - E_f - \Sigma_f(\epsilon)}}, \quad (3)$$

$$\tau_c(\epsilon)^{-1} = -2 \text{Im} \frac{V^2}{\epsilon - E_f - \Sigma_f(\epsilon)}, \quad (4)$$

where E_f and $\Sigma_f(\epsilon)$ denote the level position and the self-energy of an f-electron. V denotes the mixing and ϵ_k the energy of the conduction electrons.

The result is shown in Fig. 1 for the various f-electron level positions. The DOS of the conduction band is assumed to be a semicircular form with the half-width $W = 1$ around $\epsilon = 0$ and the resonance width of the f-level $\Delta = 0.5$. The Coulomb repulsion U between f-electrons is chosen as $U = 2$. $E_f = -1$ corresponds to the so-called symmetric case and express the Kondo insulator, and the other cases are all metallic except $E_f = -1$ and -1.2 . In the present model, the TEP can be finite only when there is an electron-hole asymmetry. The case $E_f = -1.2$ shows a steep decrease of S at low temperatures similar to the ordinary semiconductors as mentioned in §2, but $|S|$ turns to decrease linearly at lower temperatures. This is because the quasi-particle DOS, which has an energy gap of the order of the Kondo temperature

at $T = 0$, becomes strongly temperature-dependent, and the DOS in the gap becomes always finite at finite temperatures.

§4. Two-band models for FeSi and YbB₁₂

In order to understand the behavior of TEP for a specific material, it is important to start from the knowledge of a band calculation since the TEP is sensitive to the details of the electronic structure. For most of the Kondo insulators, the band calculations exhibit energy gaps at the Fermi levels. Simplest way to express these results is to use a two-band model, each of which is expressed by the DOS of the corresponding band right below and above E_F obtained from the band calculation. The mixing between f and conduction electrons is already included in these bands. Therefore, the Coulomb repulsion could have band-off-diagonal terms, even if it were diagonal in orbitals in the form of PAM. But since we do not have such knowledge at hand, we simply introduce the Coulomb interactions only within the same band and neglect the interband terms. Also, we neglect the effect of f-level degeneracy in YbB₁₂ and treat only the spin degeneracy. A full analysis including the orbital degeneracy is to be done in the next stage.

The next problem that we have to consider when we analyze the experimental data is the nonstoichiometry or impurities. Both shift the chemical potential into the conduction or valence bands. In that case, the material behaves as a metal at lowest temperatures. The experimental data for TEP of FeSi and YbB₁₂ show $S(T) \propto T$ at low temperatures. Electron-doping by Ir to FeSi leads to negative S . [6] A more careful experiment will clarify whether these are due to the nonstoichiometry/impurities or the many-body effect mentioned in §2.

First we show the results for FeSi, using the DOS calculated by Yamada. [12] Assuming the 0.01% hole-doping, we have obtained a good agreement with the experiment as shown in Fig. 2. Introduction of an intermediate value of $U = 0.5$ eV, which gives rise to reasonable agreement with the experiment on the dynamical conductivity and the specific heat, [13] changes the result only slightly since the many-body effect becomes effective only at temperatures higher than 100K in this material. [13]

Fig. 3 shows the results for YbB_{12} calculated without the correlation effect. The DOS is taken from the LDA+U band calculation by Harima[14]. The peak at 10K in the experimental curve[15] is considered to be due to the phonon-drag effect. The calculation for stoichiometric case ($n = 0$) shows a diverging upturn at lowest temperature and does not fit the experiment. The curves with 0.5% or 1% electron-doping seem to be consistent with the experiment as regards the second peak at 40K, which may be due to the f-electrons. However, the high temperature behavior is not consistent with the experiment. In YbB_{12} , the many-body effect is considered to be important at low temperatures, so that the f-part of the density of state may be strongly renormalized in its width and position, and considerably temperature-dependent. Therefore, the effective f-electron position is close to but slightly below the chemical potential at low temperatures, but it may be shifted to lower energy at temperatures higher than T_K , so that S becomes more electron-like and negative at high temperatures, improving the agreement with the experiment. Such a calculation including the correlation effect is now in progress.

§5. Discussions

It is known that the resistivity must always vanish even if there is an electron-electron or electron-phonon interactions when there is no impurity or Umklapp scatterings.[16] In contrast, the relaxation time approximation gives rise to the finite resistivity at finite temperatures. According to the Fermi liquid theory, it has been proved that the inclusion of the vertex correction results in the divergence of the conductivity correctly.[17] Detailed study of the transport coefficients for the two-dimensional Hubbard model including the Umklapp processes has been done in terms of the FLEX (fluctuation-exchange) theory.[18, 19] The effect of the Umklapp process, however, does not seem to modify the result of the relaxation time approximation at least when the anisotropy is weak. Namely, the effect of the Umklapp process seems to enhance the conductivity by a certain factor but the temperature variation may not essentially change. Therefore the results by the DMFT (correct in $d \rightarrow \infty$), which corresponds to neglecting vertex correction and Umklapp process in $d < \infty$, may be correct as regards the temperature dependence, although it might be necessary to correct the absolute values of the conductivity.

Origins of the T -linear TEP at low temperatures in FeSi and YbB₁₂ are still not clarified although we attributed them to the nonstoichiometry rather than the many-body effect in the present study. They must be uncovered by careful experimental and theoretical studies in the future.

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Figure Captions

Figure 1: The thermoelectric power of the periodic Anderson model for various values of E_f .

Figure 2: The thermoelectric power of FeSi for hole-doped case with and without Coulomb interaction is compared with the experiment.

Figure 3: The thermoelectric power of YbB₁₂ for electron-doped cases is compared with the experiment.

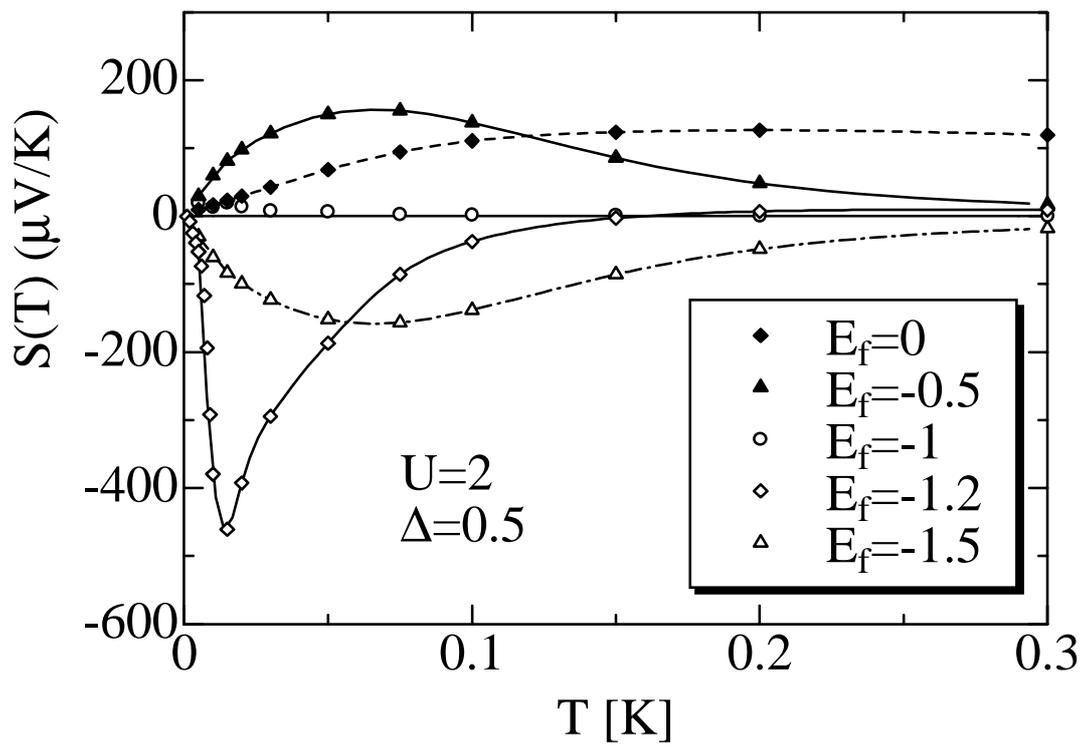


Fig.1, T. Saso, reduction 50 %

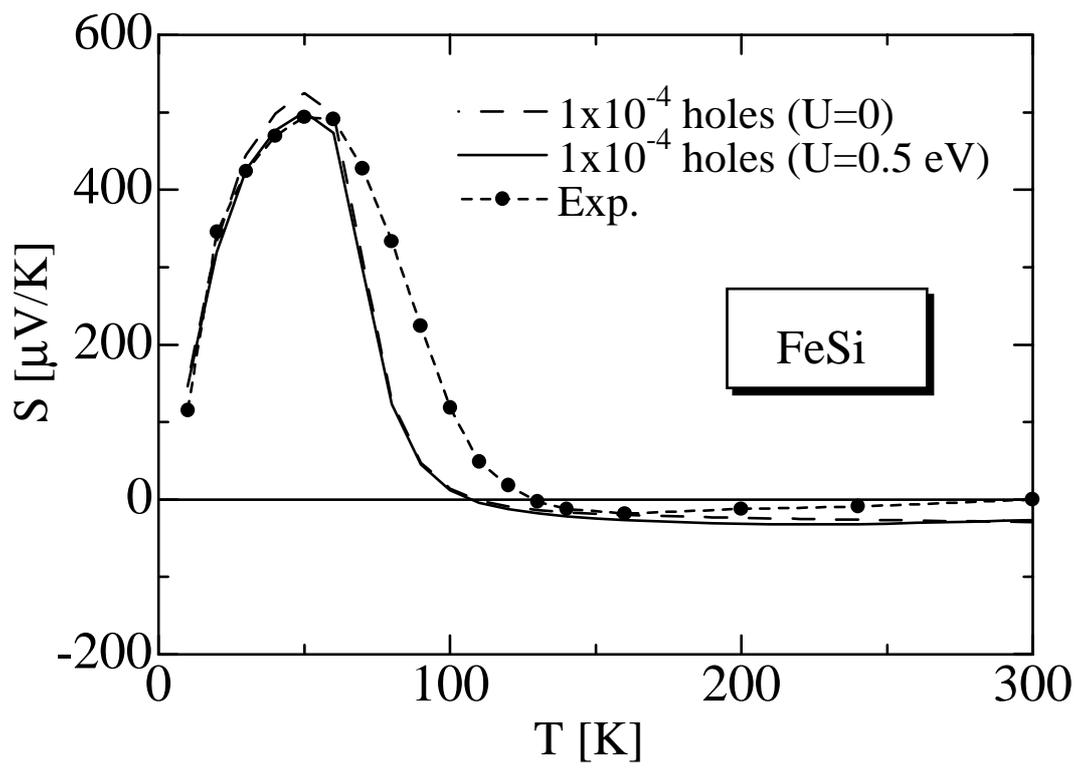


Fig.2, T. Saso, reduction 50 %

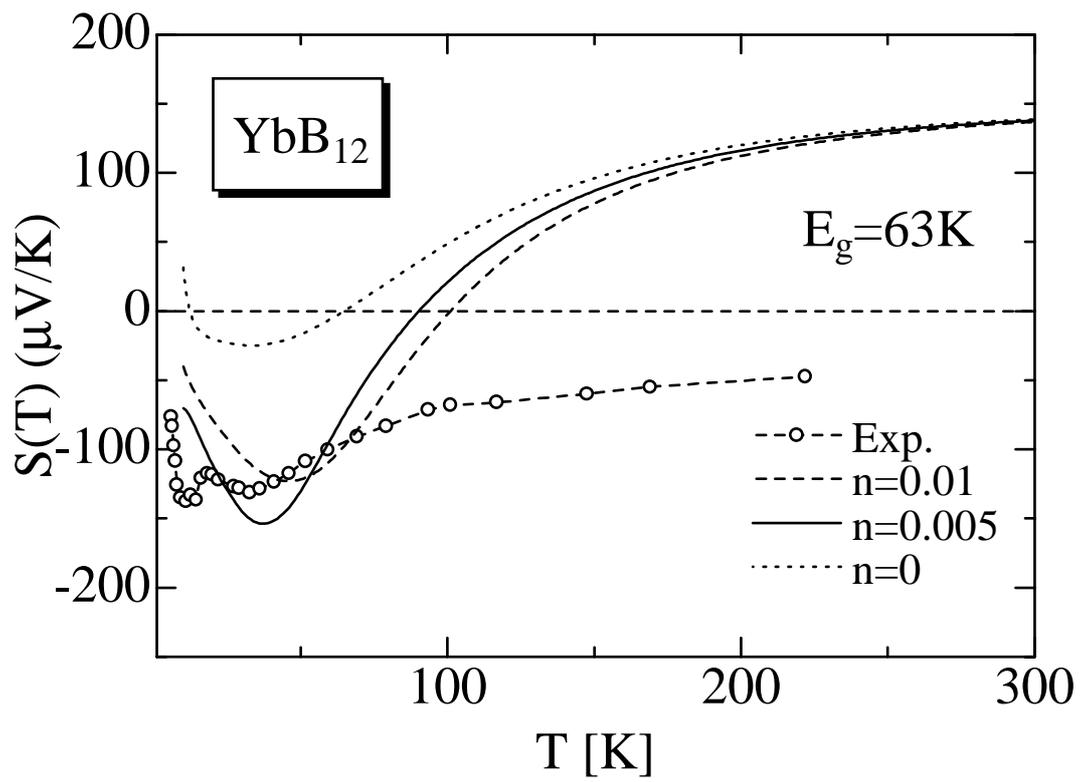


Fig.3, T. Saso, reduction 50 %