Thermoelectric Power of Kondo Insulators and Kelvin's Relations at Low Temperatures

Tetsuro Saso

Department of Physics, Saitama University
Fax: 81-48-858-3369, e-mail: saso@phy.saitama-u.ac.jp

The theory of thermoelectric effects are reinvestigated for insulators or semiconductors at low temperatures. It is found that the famous relations established by Lord Kelvin for metals in 1851 must be modified at low temperature limit of the intrinsic semiconductors in order to be consistent with the third law of the thermodynamics. Many-body effects are also discussed on the basis of Mahan's theory, and it is found that Seebeck coefficient is modified from $S(T) \propto 1/T$ to $S(T) \propto T$ at low temperatures for the Kondo insulators because the quasi-particle density of states within the gap becomes finite due to the finite life-time of electrons.

Key words: thermopower, Kelvin's relations, Kondo insulator

1. INTRODUCTION

Recently, some of the strongly correlated materials are attracting renewed interests because of a possibility for a new and efficient thermoelectric device[1]. Especially, the compounds called as the Kondo insulators[2] show rather large thermopower at low temperatures, being suitable for a refrigerator without coolant in the lower temperature range. It seems, however, that the theory for the thermoelectric effects has not yet been fully developed either for the insulators nor for the systems with strong correlation.

In this article, we will focus on the theory of the thermoelectric effect in insulators and point out for the first time that the famous Kelvin's relations, which were analyzed and established by Lord Kelvin[3] 150 years ago, must be modified for the insulators or the intrinsic semiconductors at the low temperature limit. Next, we will discuss effects of many-body interactions on the thermoelectric coefficients and give a formula for the heat current based on Mahan's theory[1]. We will also explain how the behavior of the thermopower due to the non-interacting electrons or holes in ordinary semiconductors might be changed in the Kondo insulators with strong correlations at low temperatures.
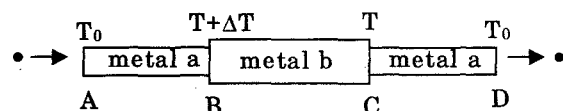

Fig.1 A schematic figure to derive Kelvin's relations. A unit positive charge is quasi-statically moved along the path ABCDA to prove Kelvin's relation.

2. RECONSIDERATION OF KELVIN'S RELATION IN INSULATORS

Lord Kelvin[3,4] analyzed a system depicted in Fig. 1 which consists of the metals a and b. The temperature difference between B and C is set equal to ΔT, and T and T_0 are the temperatures at C and A (D), respectively. (Note that the direction of the gradient is opposite to that in ref.[4]. A unit positive charge is quasi-statically

moved along the path A-B-C-D and is brought back to A. Thereby the Peltier heat $\Pi_{ab}(T+\Delta T)$ is emitted at B and $\Pi_{ab}(T)$ is absorbed at C. (Note that $\Pi_{ba}(T) = -\Pi_{ab}(T)$ is assumed here.) The Thompson heat $\tau_b \Delta T$ is emitted between B-C and $\tau_a \Delta T$ is absorbed between A-B and C-D (τ_a and τ_b denote the Thomson coefficients). On transferring the charge from D to A the work $S_{ab}\Delta T$ must be added to the electron system from the outside in order to overcome the thermoelectric voltage $\Theta_{ab} = S_{ab}\Delta T$. Thus we can set up the following equations to express the first and the second laws of the thermodynamics:

$$S_{ab}\Delta T - \Pi_{ab}(T+\Delta T) + \Pi_{ab}(T) + (\tau_a - \tau_b)\Delta T = 0, \quad (1)$$

$$-\frac{\Pi_{ab}(T+\Delta T)}{T+\Delta T} + \frac{\Pi_{ab}(T)}{T} + \frac{\tau_a - \tau_b}{T}\Delta T = 0 \quad (2)$$

and derive the famous Kelvin's relations:

$$S_{ab}(T) = \frac{\Pi_{ab}(T)}{T}, \quad S_{ab}(T) = \int_0^T \frac{\tau_a(T') - \tau_b(T')}{T'}dT' \quad (3)$$

Note that the heat or the work added to the electron system are count as positive quantities in eqs. (1) and (2).

It is well known that the absolute Seebeck coefficient is given by $S \sim -(E_c-\mu)/|e|T$ for the semiconductors at low temperatures when the carriers are electron-like, hence $S_{ab} = S_a - S_b \sim (E_c^b - E_c^a)/|e|T$. Here, E_c and μ denote the conduction band edge and the chemical potential, respectively. However, from the Kelvin's relations (3), one is forced to face the following puzzles: (A) according to the first equation in (3), one obtains $\Pi_{ab}(T \to 0) \to (E_c^b - E_c^a)/|e|$, whereas (B) S(T) must vanish at $T \to 0$ if one uses the second equation in (3). The puzzle (A) means that one can remove finite amount of heat from the body at absolute zero temperature, which seems to violate the third law of the thermodynamics.

It is possible to argue that the puzzle (B) may be resolved if one change the lower limit of integration from 0 to ∞. The puzzle (A) is more serious. But I found that it has occurred because we have neglected a work necessary to move a negative charge from the

bottom of the conduction band at E_c^a to the region in the middle with the band edge E_c^b when $E_c^b > E_c^a$ and T → 0, as shown in Fig. 2. In this case, we have to add a term $W=(E_c^b-E_c^a)/|e|$ in eq. (1) as a work explicitly, because no electrons are thermally distributed to the levels with higher energy. At finite temperatures, some numbers of electrons are thermally excited to the states above E_c^b, and can proceed to the region b without explicit work from the outside. However, at the zero temperature limit, an electron, if it is placed at the very edge of the conduction band bottom E_c^a, is not excited to the higher energy and can not move into the region b without an assist W.
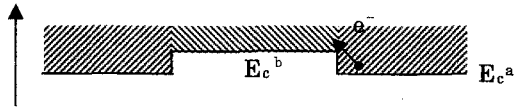

Fig.2 A schematic figure of the energy bands for three connected semiconductors a-b-a, where the hatched regions indicate the conduction bands, whereas the regions beneath them are the energy gaps. A negative charge is moved across the junction between the two semiconductors a and b with the conduction band bottom E_c^a and E_c^b, when a positive charge is moved from left to right.

It should be also necessary to point out that the relation $\Pi_{ba}(T)=-\Pi_{ab}(T)$ assumed in deriving (1) does not automatically hold here, which was overlooked in my previous analysis on this subject[5]. Thus, we assume $\Pi_{ba}(T)$ and $\Pi_{ab}(T)$ are independent of each other, and obtain

$$S_{ab}(T)\Delta T - \Pi_{ab}(T+\Delta T) - \Pi_{ba}(T) + (\tau_a - \tau_b)\Delta T + W = 0 \tag{4}$$

instead of (1). Combining (2) and (4), we can derive the following relations

$$\Pi_{ba}(T) = -TS_{ab}(T) - \frac{T}{\Delta T}W, \tag{5}$$

$$\Pi_{ab}(T+\Delta T) = (T+\Delta T)S_{ab}(T+\Delta T) + \frac{T+\Delta T}{\Delta T}W, \tag{6}$$

$$\frac{S_{ab}(T+\Delta T) - S_{ab}(T)}{\Delta T} = \frac{\tau_a - \tau_b}{T}. \tag{7}$$

Taking the limits T → 0, ΔT → T and T+ΔT → T, we finally obtain the *modified* Kelvin's relations as follows:

$$\Pi_{ba}(T) = -TS_{ab}(T), \tag{8}$$

$$\Pi_{ab}(T) = TS_{ab}(T) + W, \tag{9}$$

$$S_{ab}(T) = \int_0^T \frac{\tau_a(T') - \tau_b(T')}{T'}dT'. \tag{10}$$

In eq. (8), T must be taken as equal to 0. It should be noted that $\Pi_{ba}(T)=-\Pi_{ab}(T)$ does not hold. Instead, we have the relation $\Pi_{ba}(T)=-\Pi_{ab}(T)+W$, which can be obtained from (3) directly if one takes the limits T → 0, ΔT → T and T+ΔT → T.

Eqs. (8)-(10) can be understood if one consider how a cooling apparatus works as a thermodynamic cycle as depicted in Fig. 3. The heat which can be removed from a body connected at C (or from the lattice system of the semiconductors a and b connected at C),

$q=|\Pi_{ba}(T)|=TS_{ab}(T)$, is expected to vanish at T → 0 limit in order to be in accord with the third law of the thermodynamics, whereas the heat emitted at B is $Q=q+W=TS_{ab}(T)+W$. At zero temperature limit, we expect that this heat Q may not exceed W, which means that $TS_{ab}(T)$ → 0 at T → 0. Therefore, $q=|\Pi_{ba}(T)|=TS_{ab}(T)$ → 0 may hold instead of the ordinary formula $|\Pi_{ba}(T)|=|\Pi_{ab}(T)|=(E_c^b-E_c^a)/|e|$ even at T=0. Thus the finite value Π_{ab} → $(E_c^b-E_c^a)/|e|$ is an artifact of regarding the work to be done as the heat to be removed and the neglect of the relation $\Pi_{ba}(T) \neq -\Pi_{ab}(T)$.

Onsager's relation (the first equation of (3)) does not hold, since the linear response theory is not applicable in the present case at T → 0. Note that the equations (8)-(10) hold only at the low temperature limit and the term W should quickly disappear if the temperature is raised only slightly. A more general expression at arbitrary temperature are still to be found. Thereby, the inclusion of the nonequilibrium effects will be necessary.
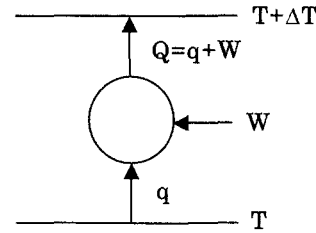

Fig.3 A schematic figure of a thermodynamic apparatus for cooling. When a work W is added to the system, a heat q is removed from the low-temperature object, and the heat Q=q+W is put out to the high-temperature one.

3. SEEBECK COEFFICIENT AND MANY-BODY EFFECT

A general theory for the thermoelectric transport has been developed by Mahan[1,6], and recently by Kontani[7] further, based on the Fermi liquid theory. It should be noted that the heat conveyed by the carriers is not equal to $\varepsilon_k-\mu$ but a correction due to the interaction exists. For example, using Mahan's theory[1], we can derive the following expression of the heat current j_Q for the Hubbard model in the second-quantized form

$$H = \sum_{k\sigma}\varepsilon_k c_{k\sigma}^+ c_{k\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow} \tag{11}$$

as

$$j_Q = \sum_{k\sigma}(\varepsilon_k - \mu)\upsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_{k\sigma}U\upsilon_k\left(c_{i\sigma}^+ c_{j\sigma}\frac{n_{i-\sigma}+n_{j-\sigma}}{2}\right)_k, \tag{12}$$

where ε_k and v_k denote the band energy and the velocity of an electron with wave vector k, $c_{k\sigma}^+$ and $c_{k\sigma}$ the creation and annihilation operators of electrons, $n_{i\sigma}=c_{i\sigma}^+c_{i\sigma}$ the number operator at site i, $(...)_k$ denotes the Fourier transformation from i,j to k and μ the chemical potential. It can be seen that the second term express the heat carried by the electrons due to the repulsive interaction U between them.

Using the linear response theory, the Seebeck

coefficient can be expressed by the following simple formula[1,7]

$$S(T) = -\frac{1}{eT}\frac{\int d\varepsilon \ (\varepsilon-\mu)L(\varepsilon)(-\frac{\partial f}{\partial \varepsilon})}{\int d\varepsilon \ L(\varepsilon)(-\frac{\partial f}{\partial \varepsilon})} \qquad (13)$$

with

$$L(\varepsilon) = \frac{1}{\pi N}\sum_{\mathbf{k}} v_{\mathbf{k}}^{2}\left[\mathrm{Im}\,G(\mathbf{k},\varepsilon)\right]^{2} \qquad (14)$$

when the vertex corrections (VC's) can be neglected, as would be the case for the heavy-fermion rare-earth compounds. VC's cannot be neglected for high T_c cuprates[7]. It should be noted that the second term in eq. (12) due to the interaction is not added to the term $(\varepsilon-\mu)$ in eq. (7). It is because all the interaction effects were absorbed in the Green's function (and in the VC's).

The electronic states of the Kondo insulators can be described most simply by the periodic Anderson model (PAM)

$$H = \sum_{\mathbf{k}\sigma}\varepsilon_{\mathbf{k}}c_{\mathbf{k}\sigma}^{+}c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\sigma}(V_{\mathbf{k}}f_{\mathbf{k}\sigma}^{+}c_{\mathbf{k}\sigma}+V_{\mathbf{k}}^{*}c_{\mathbf{k}\sigma}^{+}f_{\mathbf{k}\sigma})$$
$$+ E_{f}\sum_{i\sigma}n_{fi\sigma} + U\sum_{i}n_{if\uparrow}n_{if\downarrow} \qquad (15)$$

at half-filling. Here, the second and the third terms denote the mixing between c and f electrons and the f-electron level energy, respectively. The last term indicates the Coulomb repulsion between f-electrons. Degeneracy of the conduction bands and the f-electron states are neglected. A more realistic model is discussed in [8].

The heat current is expressed as

$$\mathbf{j}_{Q} = -\frac{i}{2}\sum_{ij\sigma}(\sum_{\ell}t_{i\ell}t_{\ell j})\mathbf{R}_{ij}c_{i\sigma}^{+}c_{j\sigma} + \sum_{ij\sigma}Vt_{ij}\mathbf{R}_{ij}(c_{i\sigma}^{+}f_{j\sigma} + H.c.)$$
$$(16)$$

for PAM in the site representation, where t_{ij} and $\mathbf{R}_{ij}$ are the hopping matrix element and the hopping vector between i and j sites, respectively. The second term does not appear in the expression for the Seebeck coefficient, and we obtain exactly the same form as (13). In (14), we have to use the conduction electron Green's function $G_c(\mathbf{k},\varepsilon)$ of PAM. The Coulomb interaction between f-electrons produces a finite imaginary part of the self-energy due to the mutual scattering at finite temperatures. This makes the quasi-particle density of states finite within the gap at T>0. Therefore, the Seebeck coefficient of the Kondo insulators becomes metal-like $S(T) \propto T$ at low but finite temperatures[9], whereas $S(T) \propto T^{-1}$ at higher temperatures.

Calculation of the f-electron self-energy $\Sigma_f(\varepsilon)$ is done using the self-consistent second-order perturbation theory combined with the local approximation in the spirit of the dynamical mean-field theory for strongly correlated electron systems[9]. Eq. (14) is evaluated approximately as $L(\varepsilon) \doteq v_c(\varepsilon)^2\rho_c(\varepsilon)\tau_c(\varepsilon)$, where v_c, ρ_c, τ_c are the velocity, the density of states and the relaxation time of conduction electrons, respectively, and are calculated from

$$\rho_c(\varepsilon) = -\frac{1}{\pi N}\mathrm{Im}\sum_{\mathbf{k}}\frac{1}{\varepsilon - \varepsilon_{\mathbf{k}} - \dfrac{V^2}{\varepsilon - E_f - \Sigma_f(\varepsilon)}} \qquad (17)$$

$$\tau_c(\varepsilon)^{-1} = -2\,\mathrm{Im}\frac{V^2}{\varepsilon - E_f - \Sigma_f(\varepsilon)} \qquad (18)$$

We have assumed that $v_c(\varepsilon)$ and $V_{\mathbf{k}}$ are independent of ε or $\mathbf{k}$. The half-width of the conduction band is taken as the unit scale of the energy. Δ denotes the resonance width of the f state, defined by $\Delta = \pi\rho_c(E_F)V^2$, where $\rho_c(E_F)$ is the density of states of the conduction band at the Fermi energy E_F. Details of the calculation will be found in [10]. Example of the numerical calculations are displayed in Fig. 4 for the parameters $U=2$, $\Delta=0.5$ and various values of E_f. $E_f=0$, -0.5 and -1.5 correspond to the metals, whereas $E_f=-1$ and -1.2 the insulators. $E_F=-1$ corresponds to the electron-hole symmetric case and $S(T)$ vanishes for all temperatures. $E_F=-1.2$ corresponds to the case of a Kondo insulator. Therefore, resistivity diverges at low temperatures. The absolute value of the Seebeck coefficient (solid line with open circles in Fig. 4) increases with decreasing temperature, which is a typical semiconducting behavior. It, however, decreases towards zero at the lower temperatures. This is due to the life-time effect originating from the many-body scattering mentioned above.
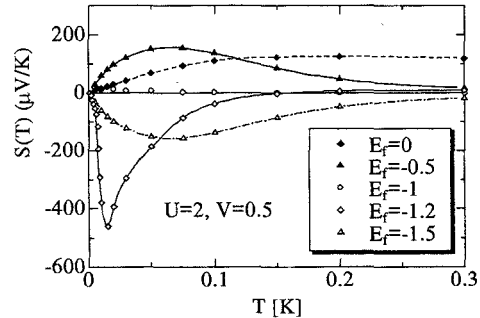

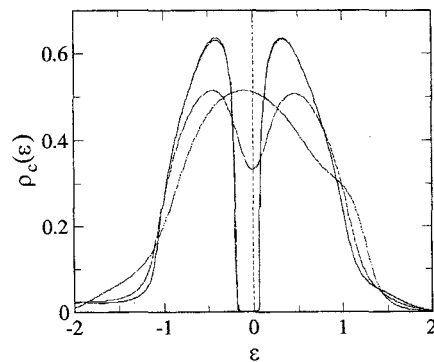Fig. 4 Seebeck coefficients for the periodic Anderson model for U=2, V=0.5 and various values of E_f.

Fig. 5 The quasi-particle density of states of conduction electrons $\rho_c(\varepsilon)$ for U=2, V=0.5, $E_F=-1.2$ and T=0, 0.03, 0.2 and 0.7.

The behaviors of $\rho_c(\varepsilon)$, $\tau_c(\varepsilon)^{-1}$ and the product $\rho_c(\varepsilon)\tau_c(\varepsilon)$, which contributes to $L(\varepsilon)$, are displayed in Figs. 5-7 for $U=2$, $V=0.5$, $E_F=-1.2$ and the temperatures $T=0$, 0.03, 0.2 and 0.7. In Fig. 5, one can see that the quasi-particle density of states of conduction electrons is strongly temperature-dependent and the gap is filled up as the temperature increases. In Fig. 6, the inverse relaxation time $\tau_c(\varepsilon)^{-1}$ is displayed, where the sharp spike at $\varepsilon\sim0$ and $T\sim0$ is due to the resonance at $E_f+\mathrm{Re}\Sigma_f(0)$, as is seen from eq.(18). The gap size in $\tau_c(\varepsilon)^{-1}$ is wider than that in $\rho_c(\varepsilon)$ because an electron needs more energy to excite an electron-hole pair in addition to the energy with which it is excited to the conduction band. The product $\rho_c(\varepsilon)\tau_c(\varepsilon)$ is displayed in Fig. 7. Although both $\rho_c(\varepsilon)$ and $\tau_c(\varepsilon)^{-1}$ vanish within the gap at $T\to0$, $\rho_c(\varepsilon)$ dominates in the behavior of $L(\varepsilon)$, and therefore, overall shape of $S(T)$ is determined mainly by $\rho_c(\varepsilon)$. In fact, $S(T)$ can be reproduced by using the approximation $L(\varepsilon)\doteqdot\mathrm{const.}\times\rho_c(\varepsilon)$. Thus, the energy dependence of $\tau_c(\varepsilon)$ is not so important in $L(\varepsilon)$.

numerically at $T\to0$. Anyhow, our prediction that $S(T)$ must vanish at low temperature limit because of the many-body effect, is qualitatively consistent with the observed behaviors[11,12], but the effect of the nonstoichiometry may not be neglected. Both interpretations seem possible for analyzing the experimental results.

4. SUMMARY

The thermoelectric effect in insulators or intrinsic semiconductors was reinvestigated theoretically. It was found that the famous relations established by Lord Kelvin for the thermoelectric coefficients must be modified at low temperature limit in order to be consistent with the third law of the thermodynamics. Many-body effect was also discussed and it was noted that new behaviors $S(T) \propto T$ or $\propto \exp(-E_g/k_BT)$ should appear at low temperatures due to the interaction effect, and might be applicable to the analysis of the Kondo insulators. To elucidate the low temperature behavior, it may be necessary to consider the nonequilibrium effect of coupled electron and phonon systems.
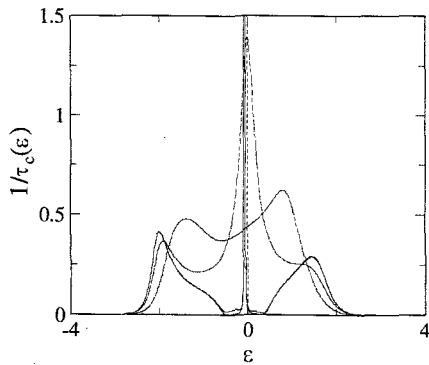
ACKNOWLEDGEMENTS

Fig. 6 The inverse relaxation time $\tau_c(\varepsilon)^{-1}$ of conduction electrons for the same temperatures as in Fig. 5 is displayed.
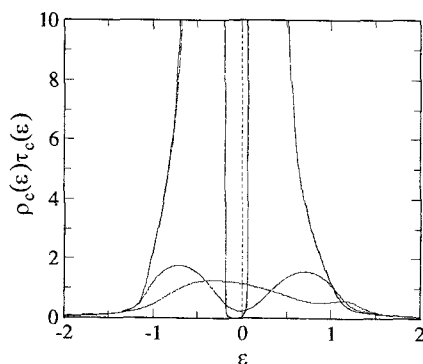

Fig. 7 The products $\rho_c(\varepsilon)\tau_c(\varepsilon)$ for the same temperatures as in Fig. 5 are displayed.

It could be the case that S vanishes as an activation type $S(T) \propto \exp(-E_g/k_BT)$ at the low temperature limit. It is not easy to discriminate between the two types of the behaviors $S(T) \propto T$ and $S(T) \propto \exp(-E_g/k_BT)$

References

[1] G. Mahan, Solid State Physics 51 (1998) 81.
[2] G. Aeppli and Z. Fisk: Comments Cond. Mat. Phys. 16 (1992) 155.
[3] W. Thomson, Proc. Roy. Soc. Edinburgh (1851) 91.
[4] A. H. Wilson, The Theory of Metals (Cambridge, 1965).
[5] T. Saso, Physica B 328 (2003) 58.
[6] M Jonson and G. D. Mahan, Phys. Rev. B 42 (1990) 9350.
[7] H. Kontani, J. Phys. Soc. Jpn. 70 (2001) 2840.
[8] T. Saso and H. Harima, J. Phys. Soc. Jpn. 72 (2003) 1131.
[9] A. Georges, G. Kotliar, W. Krauth and M. J. Rozenberg, Rev. Mod. Phys. 68 (1996) 13.
[10] T. Saso, J. Phys. Soc. Jpn. 71 Suppl. (2002) 288.
[11] F. Iga, et al., J. Mag. Magn. Mater. 226 (2001) 137.
[12] B. C. Sales, et al., Phys. Rev. B 50 (1994) 8207.