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Thermoelectric Power and Electronic Structures of Kondo Insulators

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Abstract
Thermoelectric power of the Kondo insulators is analyzed theoretically. It is pointed out that Kelvin's relation found in 1851 must be modified for insulators at low temperatures. A realistic tight-binding model is constructed for the description of the conduction bands of the most typical Kondo insulator YbB_{12}. It will be a good starting point for the development of a realistic theory of the Kondo insulators with strong correlation.

Keywords: Kondo insulator, thermoelectric power, tight-binding model

§1. Introduction

The Kondo insulator is a band insulator with strong correlation.[1, 2] There are many examples of such materials among the rare earth compounds, e.g. SmB_6, YbB_{12}, Ce_3Bi_4Pt, CeRhSb, etc.[1] FeSi is considered to be an example among the transition metal compounds.[2, 3] Recently, some of these compounds are attracting renewed interests because of a possibility for an efficient themoelectric device.[4] It seems, however, that the theory for the thermoelectric effects has not yet been fully developed for the insulators and for the systems with strong correlation.[5] In addition, quantitative analysis on these materials has been hindered because of the lack of a simple description of the basic electronic structures. LDA Band calculations on the Kondo insulators including the f-electrons as itinerant ones are carried out, giving rise to an energy gap around the Fermi energy,[6] or at least a tendency towards the opening of the gap.[7] However, the obtained band structures look rather complicated, so that a simpler tight-binding model description is necessary to explore the effect of the strong correlation starting from the band structure calculations.

In this article, we first point out that the theory of the thermoelectric effect, which was first analyzed by Lord Kelvin[8] 150 years ago and has been a standard, must be modified in the case of the insulators at low temperature limit. Next, we demonstrate that a realistic tight-binding model can be constructed for the description of the conduction bands of the most typical Kondo insulator YbB_{12}. It will be a good starting point for the development of a theory of the thermal, thermoelectric, transport and magnetic properties of the Kondo insulators with the correlation effects.

§2. Reconsideration of Kelvin's relation in insulators

Lord Kelvin[8, 9] 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. (Note that the direction of the gradient is opposite to that in ref.[9]) A unit charge is quasi-statically moved along the path ABCDA. Thereby the Peltier heat $\pi_{ab}(T + \Delta T)$ is emitted at B and $\pi_{ab}(T)$ is absorbed at C. The Thompson heat $\tau_b \Delta T$ is emitted between BC and $\tau_a \Delta T$ is absorbed between AB and CD. On transferring

the charge from D to A the work $S_{ab}\Delta T$ is done outward due to the thermoelectric voltage, where S_{ab} denotes the Seebeck coefficient. Thus we can set up the following equations to express the first and the second laws of thermodynamics:

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

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

and derive the famous Kelvin's relations:

$$S_{ab}=\frac{\pi_{ab}}{T}, \quad S_{ab}=\int_0^T \frac{\tau_a-\tau_b}{T}\mathrm{d}T. \quad (3)$$

It is well known that the absolute Seebeck coefficient is given by $S \simeq -(E_c-\mu)/|e|T$ for the semiconductors at low temperatures when the carriers are electron-like, hence $S_{ab}=S_a-S_b \simeq (E_c^b-E_c^a)/|e|T$. Here, E_c and μ denote the conduction band edge and the chemical potential, respectively. However, according to the equation (3), $\pi_{ab}(T\to 0)\to (E_c^b-E_c^a)/|e|$, whereas $S(T)$ must vanish at $T\to 0$. The former means that one can remove finite heat from the body at absolute zero temperature, violating the third law of the thermodynamics.

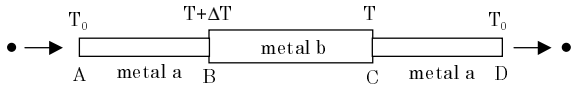

Figure 1: A unit charge is quasi-statically moved along the path ABCDA to prove Kelvin's relation.

This contradiction seems to have occurred because we have neglected the 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 $T\to 0$, 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), which leads to the modified Kelvin's relations,

$$S_{ab}=\frac{\pi_{ab}}{T}+\frac{E_c^b-E_c^a}{|e|T}, \quad (4)$$

$$S_{ab}=\int_0^T \frac{\tau_a-\tau_b}{T}\mathrm{d}T+\frac{E_c^b-E_c^a}{|e|T}. \quad (5)$$

In deriving these equations, we set $T\to 0$ and $T+\Delta T\to T$. Thus, the diverging behavior of S at low temperature limit can be understood as due to the necessary work to move a charge from the lower to the higher bottom of the conduction bands at low temperature limit. The heat which can be removed ($Q=\pi_{ab}(T)+(\tau_a-\tau_b)T$) naturally vanishes at $T\to 0$ (see Fig. 3) in this representation, and the finite value $\pi_{ab}\to (E_c^b-E_c^a)/|e|$ is an artifact of regarding the work to be done as the heat to be removed. Onsager's relation (eq.(3)) does not hold, since the linear response theory is not applicable. Equations (4) and (5) hold only at the low temperature limit and a more general expressions at arbitrary temperature are still to be found. Thereby, the inclusion of the nonequilibrium effects will be necessary.

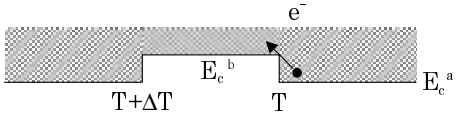

Figure 2: Motion of a negative charge through the junction between the two semiconductors with the conduction band bottom E_c^a and E_c^b, when a positive charge is moved from left to right.

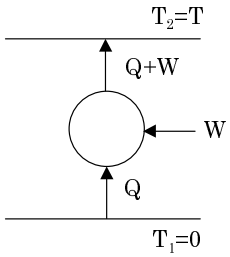

Figure 3: A schematic figure of a thermodynamic apparatus for cooling.

§3. Seebeck coefficient and many-body effect

A general theory for the thermoelectric transport has been developed by Mahan,[10] and recently by Kontani[11] further, based on the Fermi liquid theory. It should be noted that the heat conveyed by the carriers is not equal to $\epsilon_{\mathbf{k}}-\mu$ but a correction due to the interaction exists. For example, the heat current is given by

$$\boldsymbol{j}_Q = \sum_{\mathbf{k}\sigma}(\epsilon_{\mathbf{k}}-\mu)\boldsymbol{v}_{\mathbf{k}}c^+_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}$$

$$+ \quad U \sum_{\mathbf{k}\sigma} \boldsymbol{v}_{\mathbf{k}} \left(c^{+}_{i\sigma} c_{j\sigma} \frac{n_{i-\sigma} + n_{j-\sigma}}{2} \right)_{\mathbf{k}}, \quad (6)$$

for the Hubbard model, where $(\cdots)_{\mathbf{k}}$ denotes the Fourier transformation of i, j to $\boldsymbol{k}$. The Seebeck coefficient, however, can be expressed by the following simple formula

$$S(T) = -\frac{1}{|e|T} \frac{\int \mathrm{d}\epsilon (\epsilon - \mu) L(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right)}{\int \mathrm{d}\epsilon L(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right)} \quad (7)$$

with $L(\epsilon) = \sum_{\mathbf{k}} v_{x\mathbf{k}}^2 \left[\mathrm{Im} G(\boldsymbol{k}, \epsilon) \right]^2 / \pi N$ when the vertex corrections (VC's) can be neglected, as would be the case for the heavy-fermion compounds. VC's cannot be neglected for high T_c cuprates.[11] It should be noted that the second term in eq. (6) due to the interaction does not appear in the factor $(\epsilon - \mu)$ 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 at half-filling. (A more realistic model will be discussed in the next section.) The Coulomb interaction between f-electrons produces a finite imaginary part of the self-energy 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,[12] whereas $S(T) \propto T^{-1}$ at higher temperatures. This is consistent with the observed behaviors,[13, 14] but the effect of the nonstoichiometry cannot be neglected. Both interpretations seem possible for analyzing the experimental results.[12]

§4. Tight-binding model for YbB_{12}

In order to clarify the structures and the mechanisms of the energy gaps of the Kondo insulators, it is necessary to pick up a typical material with a standard and a simple structure as much as possible. YbB_{12} is the best material for such a study because it is one of the most intensively investigated materials[15, 16, 17, 18, 19] with the simple NaCl type structure, where Yb ions and B_{12} clusters are located at the interpenetrating fcc sites. Previous LDA band calculation[7] resulted in a semimetal with small overlap of the conduction and valence bands, but the recent calculation with the LDA+U method[20] does exhibit a small gap of about 0.01eV, which is due to the mixing of the 4f Γ_8 state and the conduction band of the t_{2g}character.

Whole of the electronic band seems very complicated, but if one looks at the energy dispersion curves near the Fermi level, it is possible to express the bands by the simple tight-binding model[21] with only the $(dd\sigma)$ overlapping integral between $5d\epsilon$ and $5d\gamma$ orbitals on Yb ions. This $(dd\sigma)$ should be regarded as being produced by the effective hopping through the B_{12} clusters. We take the energy levels of $5d\epsilon$ and $5d\gamma$ orbitals as $E_{d\epsilon}$=0.3 Ryd and $E_{d\gamma}$ =0.7 Ryd, respectively, and $(dd\sigma) = 0.07$ Ryd.

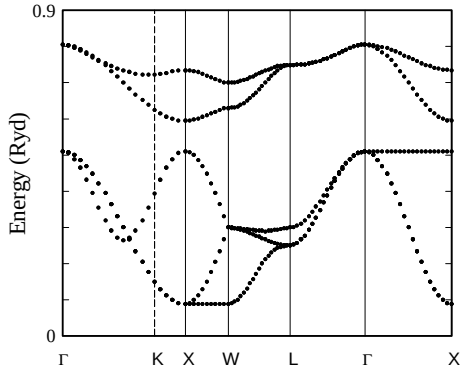

Figure 4: Tight-binding bands for the 5d conduction electrons of YbB_{12} with $E_{d\epsilon}$=0.3 Ryd, $E_{d\gamma}$ =0.7 Ryd and $(dd\sigma) = 0.07$ Ryd.

The resulting bands, shown in Fig. 4, consist of the lower $5d\epsilon$ and the higher $5d\gamma$ bands, and look very similar to the dispersions of the conduction bands of t_{2g} character near E_F in the LDA[7] and LDA+U[20] calculations, if the f states are removed. The density of states[22] for the lower band is smooth at the energy range where the 4f level is expected to be located.

It is expected that the inclusion of the 4f states at 0.15 Ryd and the mixing with the conduction bands in Fig. 1 will yield the bands with the energy gap as obtained by the LDA+U calculation[20]. However, the lowest branch in Fig.1 along Γ-X line is doubly degenerate, so that a simple mixing band model cannot yield an energy gap. One has to take account of the symmetry of the 4f states with spin-orbit interaction (Γ_8) and the conduction band (t_{2g}) properly.[7] The band calculation

does include these features and yield the energy gap. Therefore, our tight-binding band will also yield an energy gap if these features are taken into account properly. The mixing matrix elements should be given by the extended Slater-Koster integrals between d and f states.[23] Such analysis is now in progress.

§5. Conclusions

The thermoelectric effect was investigated theoretically for the Kondo insulators. Kelvin's relation for the thermoelectric effect was reconsidered and it was found that the famous relations must be modified slightly 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 commented that $S(T) \propto T$ at low temperatures due to the interaction effect. To elucidate the low temperature behavior, it may also be necessary to consider the nonequilibrium effect of electron and phonon systems.

A simple tight-binding band model was proposed for the description of the conduction bands of the most typical Kondo insulator YbB_{12}. It consists of the $5d\epsilon$ orbitals on Yb, and the overlap integral $(dd\sigma)$ is regarded as being produced by the hopping through the B_{12} clusters. This model can describe the t_{2g} conduction band very well, so that the inclusion of the mixing with the f states with proper account of the crystalline field and the spin-orbit interaction should describe the gap structure of this material correctly. The present model is very simple, so that it will be very useful in constructing a theory with correlation effect, which may consistently explain all the thermal, thermoelectric, transport and magnetic properties of YbB_{12}.[12] On the other hand, it is impossible to express the conduction band of YbB_{12} obtained from the LDA calculation by a free-electron model.[24, 25]

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