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On Thermopower and Thermal Conductivity of the Periodic Anderson Model

By

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The periodic Anderson model is used as a simple model describing intermediate-valence compounds. In that model a strong electron-electron correlation is taken into account. The correlation term is decoupled using the alloy-analogy approximation. Then the energy-dependent conductivity $\sigma(\omega)$ is obtained from the Kubo-Greenwood formula. Using $\sigma(\omega)$ the thermopower and the thermal conductivity can be calculated. For the absolute value of the thermopower a rapid increase with increasing temperature is found in the low-temperature regime with a broad maximum at mean temperatures, whereas a weak decrease occurs in the high-temperature regime. The thermal conductivity increases very rapidly with the temperature.

Das periodische Anderson-Modell wird als einfaches Modell zur Beschreibung von „Intermediate-Valence“-Verbindungen benutzt. In diesem Modell wird eine starke Elektron-Elektron-Korrelation berücksichtigt. Der Korrelationsterm wird unter Verwendung der „Legierungsanalogie“ entkoppelt. Danach gewinnt man die energieabhängige Leitfähigkeit $\sigma(\omega)$ aus der Kubo-Greenwood-Formel. Aus $\sigma(\omega)$ können Thermokraft und thermische Leitfähigkeit berechnet werden. Der Betrag der Thermokraft steigt bei niedrigen Temperaturen steil an mit einem breiten Maximum bei mittleren Temperaturen, während sie bei höheren Temperaturen wieder schwach abnimmt. Die thermische Leitfähigkeit steigt sehr stark mit der Temperatur an.

1. Introduction

In the last few years a series of papers has been concerned with various models describing intermediate-valence compounds. Within these models the electronic conductivity σ was often considered, whereas only in some papers the thermopower S and the thermal conductivity κ is calculated starting with the energy-dependent conductivity $\sigma(\omega)$. If the electronic conductivity $\sigma(\omega)$ of the model is known, it is possible to define a distribution function

$$L(\omega) = \left(-\frac{\partial}{\partial \omega} \frac{1}{e^{\beta(\omega-\mu)} + 1} \right) \sigma(\omega). \quad (1)$$

$L(\omega)$ is connected with the electrical conductivity σ by

$$\sigma = \int_{-\infty}^{+\infty} d\omega L(\omega). \quad (2)$$

Now the momenta L_n of this distribution can be evaluated [1], according to

$$L_n = \frac{1}{e^2} \int_{-\infty}^{+\infty} d\omega L(\omega) (\omega - \mu)^n. \quad (3)$$

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Then the thermopower S is given by

$$S = \frac{1}{eT} \frac{L_1}{L_0} \quad (4)$$

and the thermal conductivity κ follows from

$$\kappa = \frac{1}{T} \left(L_2 - \frac{L_1^2}{L_0} \right). \quad (5)$$

In the present paper the periodic Anderson model is used to get a reasonable expression for $\sigma(\omega)$, since in that model the influence of the electron correlation being of importance in real intermediate-valence compounds can be studied [2, 3].

2. Model and Approximations

The Hamiltonian of the periodic Anderson model is given by

$$H = H^d + H^f + H^{fd} \quad (6)$$

with

$$H^d = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} d_{\mathbf{k}\sigma}^{\dagger} d_{\mathbf{k}\sigma}, \quad (7)$$

$$H^f = \sum_{i\sigma} (E_0 f_{i\sigma}^{\dagger} f_{i\sigma} + \frac{1}{2} U f_{i\sigma}^{\dagger} f_{i\sigma} f_{i-\sigma}^{\dagger} f_{i-\sigma}), \quad (8)$$

$$H^{fd} = \frac{V}{\sqrt{N}} \sum_{i\mathbf{k}\sigma} (e^{i\mathbf{k}\mathbf{R}_i} d_{\mathbf{k}\sigma}^{\dagger} f_{i\sigma} + \text{h.c.}). \quad (9)$$

The notation is the same as in [3]. H^d describes the d-electron band in the nearly-free-electron approximation, H^f is the Hamiltonian of the localized f-electrons, and H^{fd} contains the hybridization. For more detailed information and discussion see [2 to 5].

Since the model includes the electron-electron interaction U , approximations are necessary. Here the alloy analogy [6] is used, which is particularly appropriate [2]. Within this method a stochastic potential $E_{i\sigma}$ approximates the electron-electron scattering of an f-electron with spin σ due to an electron with spin $-\sigma$. $E_{i\sigma}$ assumes two values, $(E_0 + U)$ with the probability $n_{-\sigma}^f$ and E_0 with the probability $(1 - n_{-\sigma}^f)$, according to the fact, whether a $(-\sigma)$ -electron is situated at the lattice site \mathbf{R}_i or not. n_{σ}^f is defined by

$$n_{\sigma}^f = \langle f_{i\sigma}^{\dagger} f_{i\sigma} \rangle \quad (10)$$

and has to be calculated self-consistently.

Now the Hamiltonian (6) is treated using a generalized CPA [6, 3, 5], which results an effective CPA one-particle Green function for the d- and f-electrons:

$$G_{\sigma dd}^{\text{CPA}}(\mathbf{k}, \omega) = \frac{\omega - \varepsilon_{\mathbf{k}}^d}{(\omega - \varepsilon_{\mathbf{k}}^d)(\omega - W_{\sigma}^f) - V^2}, \quad (11)$$

$$G_{\sigma ff}^{\text{CPA}}(\mathbf{k}, \omega) = \frac{\omega - W_{\sigma}^f}{(\omega - \varepsilon_{\mathbf{k}}^d)(\omega - W_{\sigma}^f) - V^2}, \quad (12)$$

where W_{σ}^f is the energy-dependent effective complex potential, fulfilling the equation

$$W_{\sigma}^f = E_0 + n_{-\sigma}^f U + (E_0 - W_{\sigma}^f) G_{ff\sigma}^{\text{CPA}}(\omega) (W_{\sigma}^f - E_0 - U), \quad (13)$$

where $G_{ff\sigma}^{\text{CPA}}(\omega)$ is defined in (16).

The CPA equation (13) can be solved by an iterative procedure, used already in [3].

Thereby, the electron densities n_σ^f and n_σ^d are given by

$$n_\sigma^f = \int_{-\infty}^{+\infty} d\omega \frac{1}{e^{\beta(\omega-\mu)} + 1} D_\sigma^f(\omega), \quad (14)$$

$$n_\sigma^d = \int_{-\infty}^{+\infty} d\omega \frac{1}{e^{\beta(\omega-\mu)} + 1} D_\sigma^d(\omega) \quad (15)$$

with

$$D_\sigma^f(\omega) = -\frac{1}{\pi} \text{Im} G_{\text{off}}^{\text{CPA}}(\omega), \quad G_{\text{off}}^{\text{CPA}}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} G_{\text{off}}^{\text{CPA}}(\mathbf{k}, \omega), \quad (16)$$

$$D_\sigma^d(\omega) = -\frac{1}{\pi} \text{Im} G_{\text{odd}}^{\text{CPA}}(\omega), \quad G_{\text{odd}}^{\text{CPA}}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} G_{\text{odd}}^{\text{CPA}}(\mathbf{k}, \omega). \quad (17)$$

The chemical potential μ has to be calculated from the equation

$$n = n^f + n^d = \sum_{\mathbf{k}} \int_{-\infty}^{+\infty} d\omega \frac{1}{e^{\beta(\omega-\mu)} + 1} D_\sigma(\omega); \quad D_\sigma(\omega) = D_\sigma^f(\omega) + D_\sigma^d(\omega). \quad (18)$$

Equations (11) to (18) form a self-consistent set.

After replacing the correlation term in (8) by the coherent potential W_σ^f , the resulting bilinear form of the effective Hamiltonian allows to compute the energy-dependent conductivity $\sigma(\omega)$ using the Kubo-Greenwood formula. Due to the \mathbf{k} -independence of the hybridization and the strong localization of f-electrons only d-electrons contribute to the electrical current. Therefore, $\sigma(\omega)$ is given by

$$\sigma(\omega) = \frac{e^2}{3\pi\Omega_0} \frac{1}{N} \sum_{\mathbf{k}, \sigma} \left(\frac{\partial \varepsilon_{\mathbf{k}}^d}{\partial \mathbf{k}} \right)^2 (\text{Im} G_{\text{odd}}^{\text{CPA}}(\mathbf{k}, \omega))^2. \quad (19)$$

For simplification of the numerical calculation some additional approximations are introduced. For the density of states $D^0(\omega)$ of the unperturbed d-electron band a simple semielliptical shape is used,

$$D^0(\omega) = \frac{2}{\sqrt{\pi}} \sqrt{1 - \omega^2} \theta(1 - |\omega|). \quad (20)$$

Thereby, the half d-bandwidth w^d chosen as unity scales the energy. Furthermore the velocity function in (19) is approximated by [7, 8]

$$\left(\frac{\partial \varepsilon_{\mathbf{k}}^d}{\partial \mathbf{k}} \right)^2 = \frac{1}{m^*} (1 - \varepsilon_{\mathbf{k}}^{d2}) \theta(1 - |\varepsilon_{\mathbf{k}}^d|), \quad (21)$$

where m^* is the effective mass of the d-electrons. If only the paramagnetic case is considered, the closed expression

$$\sigma(\omega) = \frac{e^2}{12\pi m^* \Omega_0} \left(6 - \frac{\pi D_\sigma^d(\omega)}{\text{Im}(V^2/(\omega - W_\sigma^f))} \right) (\pi^2 D_\sigma^d(\omega))^2 \quad (22)$$

follows by analytical integration [9, 3].

The thermopower S and the thermal conductivity κ can be obtained now from (1), (3) to (5) using $\sigma(\omega)$ from (22). It should be mentioned that to calculate $\sigma(\omega)$ the self-consistent computation of W_σ^f , μ , and n_σ^f has to be carried out ((13), (14), and (18)).

3. Numerical Results and Discussion

The numerical computations are based on the calculations described in [3]. For the numerical procedure reasonable values of parameters E_0 , U , V , and n are needed. The energy scale is defined by the choice of the half bandwidth w^d , as mentioned above. Due to the electron-electron correlation U the f-band splits into two subbands. The typical mixed-valence situation is reached if one of these f-split bands is placed near the centre of the d-band. In the calculations presented here the lower f-band is considered to overlap with the d-band. If n is chosen in such manner that the chemical potential μ is situated near the position of the f-level, a strong temperature dependence of the electronic transport coefficients has to be expected due to the temperature shift of the chemical potential μ through a rather quickly changing value of the density of states $D_\sigma(\omega)$. This situation occurs if $n = 1$ or $n = 2$ connected with $E_0 < 0$ or $n = 2$ or $n = 3$ with $E_0 > 0$ is chosen, whereas the strength of the correlation energy U is assumed as 3 or 2. For the \mathbf{k} -independent hybridization matrix element V the value 0.1 is used, since at higher values of V the localized character of the f-electrons vanishes. On the other hand, V should not be too small to get essential effects from the f-scattering on the transport quantities.

The densities of states $D_\sigma(\omega)$ resulting from the used sets of parameters are extensively discussed in [3]. There interesting gap structures were observed caused by the combined influence of the densities of states on n_σ^f . It should be noticed that the same structures are obtained by Schweitzer and Graham [10], although they considered the case of infinite U , which is an additional argument for the rather weak U dependence of the electronic properties of the used model (if $U > w^d$) claimed in [3]. On the other hand, Czycholl and Leder [5] got results for $D_\sigma(\omega)$ which differ from [3]. A possible reason for this disagreement could be that in [5] the self-consistency in computing n_σ^f is not taken into account carefully, since in [5] the upper f-level is considered to overlap with the d-band, so the occupation of the lower f-level depending on n_σ^f is of importance, whereas in [3] this difficulty is avoided because the upper f-level is empty.

The influence of the detailed gap structure on the general behaviour of the thermopower S and the thermal conductivity α is of less importance, if the chemical potential

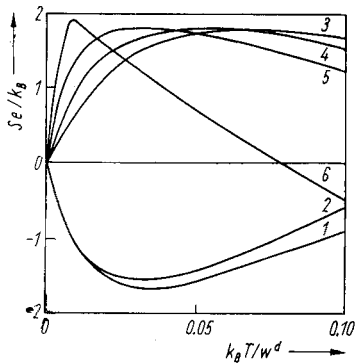


Fig. 1

Fig. 1. Thermopower S vs. temperature T for different sets of parameters. $(E_0 | U | V | n) =$ (1) (0.0 | 3.0 | 0.1 | 2), (2) (0.0 | 2.0 | 0.1 | 2), (3) (0.0 | 3.0 | 0.1 | 1), (4) (-0.1 | 3.0 | 0.1 | 1), (5) (-0.25 | 3.0 | 0.1 | 1), (6) (-0.5 | 3.0 | 0.1 | 1)

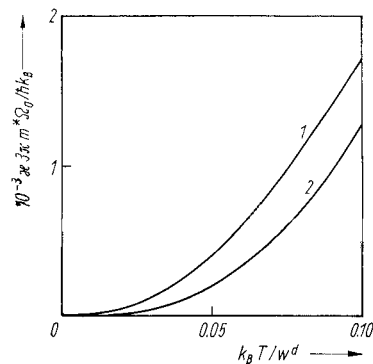


Fig. 2

Fig. 2. Thermal conductivity α vs. temperature T for two sets of parameters $(E_0 | U | V | n) =$ (1) (0.1 | 3.0 | 0.1 | 2), (2) (-0.1 | 3.0 | 0.1 | 1)

μ is situated outside the gap region, which results for the parameters used in the present-ed calculations and also for the case considered by Czycholl and Leder [5].

In Fig. 1 the thermopower S is plotted versus the temperature T for various sets of parameters. The two curves with $n = 2$, $E_0 = 0$, $V = 0.1$ and $U = 3$, $U = 2$, respectively, support the weak U -dependence mentioned above. The curves with $n = 1$, $U = 3$, $V = 0.1$, and different E_0 demonstrate, that the maximum becomes sharper and tends to lower temperatures T if E_0 decreases. By decreasing E_0 the chemical potential μ shifts to the lower split peak and, therefore, the sign of the thermopower will be changed. Unfortunately, the numerical accuracy of the curves with $E_0 = -0.25$, -0.5 is not very high due to the difficulties to reach convergence of the self-consistent procedure for W_σ^f , n_σ^f , and μ . The behaviour of the calculated thermopower S agrees qualitatively with experimental results for some Ce compounds (simulated by $n = 1$) [11] and Yb compounds (simulated by $n = 2$) [12].

The thermal conductivity κ increases very rapidly with increasing temperatures, as demonstrated in Fig. 2. For temperatures T with $k_B T/w^d > 0.10$ the computed values of κ are proportional to T^α with $\alpha \approx 2.3$ for $E_0 = -0.1$ (curve 2) and $\alpha \approx 3.0$ for $E_0 = 0.1$ (curve 1), respectively. The Wiedemann-Franz law is not fulfilled.

The qualitative behaviour of the thermopower S versus the temperature T for the considered model shows the same tendency for all sets of parameters used here. The shapes of the curves are not strongly dependent on the fine structure of the gap region in the chosen cases, since the chemical potential μ is outside the gap region.

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References

- [1] G. BUSCH and H. SCHADE, Vorlesung über Festkörperphysik, Birkhäuser-Verlag, Basel 1973 (p. 359).
- [2] N. GREWE, H. J. LEDER, and P. ENTEL, Festkörperprobleme **20**, 413 (1980).
- [3] K. ELK, phys. stat. sol. (b) **105**, 507 (1981); (b) **107**, 387 (1981).
- [4] L. M. FALICOV, W. HANKE, and M. P. MAPLE (Ed.), Valence Fluctuations in Solids, North-Holland Publ. Co., Amsterdam 1981.
- [5] G. CZYCHOLL and H. J. LEDER, Z. Phys. B **44**, 59 (1981).
- [6] B. VELICKY, S. KIRKPATRICK, and H. EHRENFELCH, Phys. Rev. **175**, 747 (1968).
- [7] B. VELICKY, Phys. Rev. **184**, 614 (1969).
- [8] M. BRAUWERS, A. K. BHATTACHARYA, and F. BROUERS, J. Phys. F **6**, 209 (1976).
- [9] A.-B. CHEN, G. WEISZ, and A. SHER, Phys. Rev. B **5**, 2897 (1972).
- [10] J. W. SCHWETZER and R. L. GRAHAM, J. appl. Phys. **52**, 2146 (1981).
- [11] D. JACCARD and J. SIERRO, Proc. Internat. Conf. Valence Instabilities, Zürich, April 13 to 16, 1982 (p. 97).
- [12] H. STHIOUL, D. JACCARD, and J. SIERRO, *ibid.* (p. 219).

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