Temperature Dependence of the Thermopower

of the Periodic Anderson Model

By

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In a previous paper the thermopower S and the thermal conductivity $\varkappa$ of the periodic Anderson model, describing mixed valence compounds, was investigated neglecting the influence of phonons /1/. Now phonons are introduced using a modified version of the model of Chen, Weisz, and Sher /2, 3/ describing the electron-phonon scattering by a temperature dependent stochastic potential. The Hamiltonian is given by

$$H = H_{PAM} + H_{CWS} \, , \tag{1}$$

whereas H_{PAM} is the same operator as used in /3/, i.e.

$$H_{PAM} = \sum_{k\sigma} \varepsilon_{\vec{k}} d^+_{\vec{k}\sigma} d_{\vec{k}\sigma} + \sum_{i\sigma} (E_o f^+_{i\sigma} f_{i\sigma} + \frac{U}{2} f^+_{i\sigma} f_{i\sigma} f^+_{i-\sigma} f_{i-\sigma}) +$$

$$+ \frac{V}{\sqrt{N}} \sum_{i\vec{k}\sigma} (e^{i\vec{k}\vec{R}_i} d^+_{\vec{k}\sigma} f_{i\sigma} + h.c.) \, . \tag{2}$$

H_{PAM} takes into account the contribution of the d-electrons in a nearly free electron approximation, the localised f-electrons, the interaction between f-electrons with different spins at the lattice site i, and the hybridisation between f- and d-electrons. The notation is in agreement with /3, 1/.

H_{CWS} is given by

$$H_{CWS} = \sum_i \Theta_i f^+_{i\sigma} f_{i\sigma} \tag{3}$$

and includes the stochastically fluctuating term Θ_i simulating the potential deformations due to phonons ("thermal disorder"). Of course this is a rather crude approximation of the electron-phonon scattering. However, this model

1) Friedrich-List-Platz 1, DDR-8010 Dresden, GDR.

produces a fairly good description of disordered alloys /4/ - a problem, which is analogous in some sense especially if the alloy analogy is explicitly used. Since the stochastic potential parameters Θ_i in (3) should simulate thermal fluctuations a continuous distribution $P(\Theta)$ is assumed. Chen et al. /2/ discuss a Gaussian distribution, which can be verified starting from the Fröhlich Hamiltonian. Since we believe the detailed shape of the distribution to be of weak influence, what is reasonable for the case where the chemical potential μ is centered in the d-band, a Lorentzian distribution is assumed for mathematical advantages /3, 4/:

$$P(\Theta) = \frac{1}{\pi} \frac{\Delta}{\Theta^2 + \Delta^2} \; ; \quad \Delta = \Delta(T) \quad . \tag{4}$$

In (3) the phonons act on the f-electrons, whereas the phonon-d-electron interaction is neglected, what is reasonable if Δ is much smaller than the width of the d-band.

The phonon independent part of the Hamiltonian H_{PAM} is replaced by a non-interacting hybridized two-band system by using the alloy analogy to decouple the electron-electron correlation. The remaining Hamiltonian together with H_{CWS} can be solved by a generalized CPA procedure /5, 6/. For this a coherent potential W_σ is introduced to form the effective Hamiltonian

$$H_{CPA} = \sum_{\vec{k}\sigma} \left\{ \varepsilon_{\vec{k}} d^+_{\vec{k}\sigma} d_{\vec{k}\sigma} + (W_\sigma + \Theta) f^+_{\vec{k}\sigma} f_{\vec{k}\sigma} + V(d^+_{\vec{k}\sigma} f_{\vec{k}\sigma} + f^+_{\vec{k}\sigma} d_{\vec{k}\sigma}) \right\} . \tag{5}$$

Here $f^+_{\vec{k}\sigma} (f_{\vec{k}\sigma})$ are the Fourier transforms of the $f^+_{i\sigma} (f_{i\sigma})$.

In a single site approximation W_σ is to evaluate from the "thermal" averaged CPA equation

$$\tilde{\tau}_i = \int_{-\infty}^{+\infty} d\Theta\, P(\Theta) \left(n^f_{-\sigma} \frac{E_0 + \Theta + U - W_\sigma}{1 - (E_0 + \Theta + U - W_\sigma) G^{ff}_\sigma(\omega)} \right.$$

$$\left. + (1 - n^f_{-\sigma}) \frac{E_0 + \Theta - W_\sigma}{1 - (E_0 + \Theta - W_\sigma) G^{ff}_\sigma(\omega)} \right) = 0 \quad , \tag{6}$$

with $G^{ff}_\sigma(\omega)$ being the Green function

$$G^{ff}_\sigma(\omega) = \frac{1}{N} \sum_{\vec{k}} \frac{\omega - \varepsilon^d_{\vec{k}}}{(\omega - \varepsilon^d_{\vec{k}})(\omega - W_\sigma) - V^2} \quad . \tag{7}$$

Furthermore we have

$$G_\sigma^{dd}(\omega) = \frac{1}{N} \sum_{\vec{k}} \frac{\omega - W_\sigma}{(\omega - \varepsilon_{\vec{k}}^d)(\omega - W_\sigma) - V^2} \ . \tag{8}$$

From (7) and (8) we get the density of states in the usual way by

$$D_\sigma(\omega) = D_\sigma^d(\omega) + D_\sigma^f(\omega) = -\frac{1}{\pi} \mathrm{Im}(G_\sigma^{ff}(\omega) + G_\sigma^{dd}(\omega)) \ . \tag{9}$$

To solve (6) the particle density n_σ^f is needed. It is available from $D_\sigma^f(\omega)$ by

$$n_\sigma^f = \int_{-\infty}^{+\infty} d\omega \frac{1}{e^{\beta(\omega - \mu)} + 1} D_\sigma^f(\omega) \ , \tag{10}$$

where μ is the chemical potential. μ can be calculated from the implicit equation

$$n = \sum_\sigma \int_{-\infty}^{+\infty} d\omega \frac{1}{e^{\beta(\omega - \mu)} + 1} D_\sigma(\omega) \ . \tag{11}$$

The Θ-integration in (6) can be carried out, if

$$\mathrm{sgn}\left\{ \mathrm{Im} \left[W_\sigma + G_\sigma^{ff}(\omega)^{-1} \right] \right\} = +1 \tag{12}$$

is valid. Lloyd /7/ has proved this relation for a one-band model. A generalisation of his ideas shows that this condition is fulfilled also for the here considered two-band model /8/. Making use of this fact the Θ-integration in (6) becomes

$$0 = n_{-\sigma}^f \frac{E_0 + U + i\Delta - W_\sigma}{1 - (E_0 + U + i\Delta - W_\sigma)G_\sigma^{ff}(\omega)} + \left(1 - n_{-\sigma}^f \frac{E_0 + i\Delta - W_\sigma}{1 - (E_0 + i\Delta - W_\sigma)G_\sigma^{ff}(\omega)} \right) \ . \tag{13}$$

Adding W_σ on both sides W_σ can be calculated by a fast iteration procedure if n_σ^f is calculated self-consistently from (10). For the unperturbed density of states of the d-electrons a semielliptical shape is assumed. ·In that way the $\vec{k}$-sums in (7) and (8) can be changed into an ε-integration /3/.

Equations (13), (7), (8), (10), and (11) form a difficult self-consistent problem. It was solved for the paramagnetic case with the same numerical procedures employed in /3, 1/. Then the energy dependent conductivity $\sigma(\varepsilon)$ can be calculated from the density of states using the Kubo-Greenwood formula /3/. The thermopower S and the thermal conductivity $\varkappa$ can be obtained from the energy moments of the distribution function $L(\varepsilon)$ including $\sigma(\varepsilon)$ and the
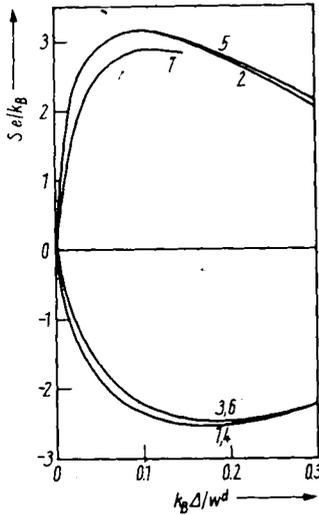
Fig. 1. Thermopower S versus distribution parameter Δ ($\alpha = 1$) for different sets of parameters $(E_c |U| V| n) = (1) (0.0|2.0|0.1|1)$, (2) $(0.0|2.0|0.03|2)$, (3) $(0.0|2.0|0.03|1)$, (4) $(0.0|3.0|0.1|1)$, (5) $(0.0|3.0|0.03|2)$, (6) $(0.0|3.0|0.03|1)$, (7) $(0.0|3.0|0.1|2)$

derivative of the Fermi function. The moments L_n are defined by

$$L_n = \frac{1}{e^2} \int_{-\infty}^{+\infty} d\varepsilon \, L(\varepsilon)(\varepsilon - \mu)^n \tag{14}$$

with

$$L(\varepsilon) = \left(-\frac{\partial}{\partial \varepsilon} \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}\right) \sigma(\varepsilon) \tag{15}$$

and $\sigma(\varepsilon)$ being

$$\sigma(\varepsilon) = \frac{e^2}{12\pi m^* \Omega_0} D_\sigma^{d2}(\varepsilon) \left(6 - \frac{\pi D_\sigma^d(\varepsilon)}{\mathrm{Im}(V^2/(\varepsilon - W_\sigma))}\right) \tag{16}$$

The thermopower S and the thermal conductivity $\varkappa$ are given by

$$S = \frac{1}{eT} \frac{L_1}{L_0} \tag{17}$$

and

$$\varkappa = \frac{1}{T}(L_2 - L_1^2/L_0) \ . \tag{18}$$

As a first step the thermopower was calculated in dependence of the distribution parameter Δ in (4). The deformation of the Fermi function due to temperature was neglected in order to study purely the influence of thermal disorder. Furthermore the temperature was assumed as linearly dependent on the distribution parameter Δ, i.e.
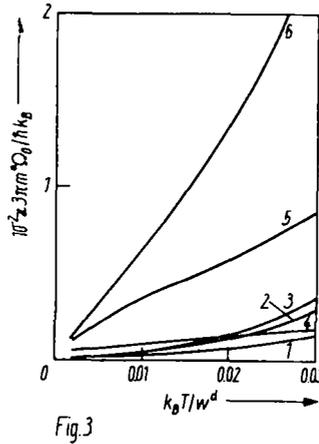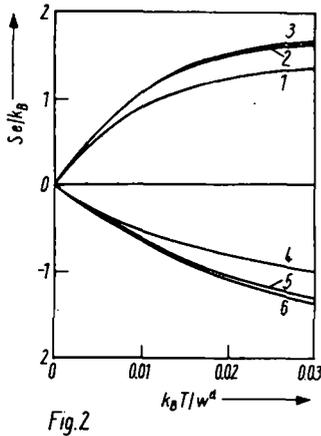
Fig.2

Fig.3

Fig. 2. Thermopower S versus temperature T for different values of $\alpha = T/\Delta$ $(E_0$ U V n) $\alpha =$ (1) (0.0 3.0 0.1 2) 1, (2) (0.0 3.0 0.1 2) 10, (3) (0.0 3.0 0.1 2) 100, (4) (0.0 3.0 0.1 1) 1, (5) (0.0 3.0 0.1 1) 10, (6) (0.0 3.0 0.1 1) 100

Fig. 3. Thermal conductivity $\varkappa$ versus temperature T for the same sets of parameters as in Fig. 2

$$T = \alpha \Delta .$$

(19)

Then the thermopower S can be obtained from Mott's formula

$$S = \frac{R^2}{3e} \alpha \Delta \frac{1}{\sigma(\epsilon_F)} \left(\frac{d\sigma(\epsilon)}{d\epsilon} \right)_{\epsilon = \epsilon_F} .$$

(20)

In Fig. 1 the thermopower S versus the distribution parameter is plotted for different sets of parameters. The thermopower shows a similar dependence on Δ as in /1/ on the temperature since the shift of ϵ_F due to an increase of Δ produces the same effect as the shift of μ by increasing temperature. This fact can be understood, since the effective Hamiltonian (5) is a sum over one-particle Hamiltonians with f-potentials at different sites i fluctuating around E_0, that means the f-electron states are distributed according to $P(\Theta)$ with the centre at E_0. Therefore the top of the peak in the f-electron density of states will be lowered and the flank states will get higher weight if the distribution parameter Δ will be increased.

This Δ-induced broadening of the peak in the f-density of states shifts a part of the f-states into the region below ε_F. These new f-states will be occupied by d-electrons. In this way n^f grows whereas ε_F decreases. n^f changes also in the same direction as it happens in /1/ and /3/ due to temperature.

In additional calculations the influence of the temperature on the Fermi function is fully taken into account. In Fig. 2 the thermopower S of different sets of parameters is plotted with different values of α. Since both the phonons and the temperature act in the same direction qualitatively new curves were not to expect. In Fig. 3 the thermal conductivity $\varkappa$ is plotted for the same parameter sets as in Fig. 2.

The author is indebted to Prof. Dr. K. Elk and Dr. J. Richter for helpful hints and discussion.

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