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Thermoelectric Power in Dilute Magnetic Alloys

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Making use of the spin independent scattering amplitude $t(\omega)$ of the conduction electrons due to a magnetic impurity for the *s-d* exchange interaction, we calculate the thermoelectric power of the dilute alloy system.

A large thermoelectric power in a dilute alloy of noble metals containing a small amount of magnetic impurities has been considered by several authors[1)-3)] on the basis of the *s-d* exchange model. Kondo[1)] calculated the thermoelectric power by expanding the scattering amplitude in powers of J, the exchange potential. In particular he points out the importance of the ordinary potential term V in accounting for the large thermoelectric power so far observed.[4)] Some errors in Kondo's calculation were corrected later by a more careful work of Fischer.[2)] More recently making use of the t matrix obtained from Suhl's dispersion equation, Suhl and Wong[3)] presented a number of theoretical curves valid at all temperatures. Their results seem to explain qualitatively the gross feature of the thermoelectric power observed in dilute alloys.[4)] Since then the closed form solution of Suhl's equation (or Nagaoka's equation) for the scattering matrix was found,[5)~9)] and it is possible to express the thermoelectric power in an analytical form.

We would like to present in this note a simple expression for the thermoelectric power, which is, we hope, more convenient in analysis of the experimental data. As usually done in the problem of a magnetic impurity, we assume that the scattering of the conduction electron due to the magnetic impurity is described by a following hamiltonian:

$$H_V = \psi_\alpha^+(0)\,(V\delta_{\alpha\beta} + \tfrac{1}{2}J\boldsymbol{S}\cdot\boldsymbol{\sigma}_{\alpha\beta})\,\psi_\beta(0), \tag{1}$$

where V and J are constants. We took here the position of the impurity as the origin.

The spin independent scattering amplitude $t(\omega)$ within Suhl's scheme[1)] (or Nagaoka's[10)]) is given[11)] as

$$t(\omega) = \frac{1}{2\pi i\rho}\left\{1 - e^{2i\eta + i\Delta(\omega)}\frac{X(\omega)}{[X^2(\omega) + \pi^2 s(s+1)]^{1/2}}\right\}, \tag{2}$$

$$X(\omega)=\ln\frac{T}{T_K}+\psi\left(\frac{1}{2}-\frac{i\omega}{2\pi T}\right)-\psi\left(\frac{1}{2}\right),$$

$$\Delta(\omega)=\frac{1}{2\pi i}\int\frac{dx}{\omega-x+i\delta}\ln|H(x)|,$$

$$H(x)=\frac{|X(x-i\delta)|^2+\pi^2 s(s+1)}{X(x-i\delta)^2+\pi^2 s(s+1)},$$

$$e^{2i\eta}=\frac{1+i(\pi\rho V)}{1-i(\pi\rho V)},\qquad T_K=\frac{2\gamma D}{\pi}\exp\left(-\frac{1}{\rho|\tilde{J}|}\right)$$

and

$$\tilde{J}=J\cos^2\eta, \tag{3}$$

where $\psi(z)$ is the di-gamma function, ρ is the density of state at the Fermi surface and η is the phase shift due to the ordinary potential V only. In the following consideration we neglect $\Delta(\omega)$, since we can show that this factor is of little importance in the discussion of the transport properties.

In terms of $t(\omega)$ given in (2), we can express the thermoelectric effect as

$$\mathfrak{S}=\frac{1}{eT}\frac{L_1}{L_0}, \tag{4}$$

$$\begin{aligned}L_0&=\int_{-D}^{D}\frac{d\omega}{2T}\phi(\omega)\cosh^{-2}\left(\frac{\omega}{2T}\right),\\ L_1&=\int_{-D}^{D}\frac{d\omega}{2T}\omega\phi(\omega)\cosh^{-2}\left(\frac{\omega}{2T}\right)\end{aligned} \tag{5}$$

and

$$\phi(\omega)=\frac{\rho(\omega)v^2(\omega)}{12\pi^2}[-2c\,\mathrm{Im}\,t(\omega)]^{-1}, \tag{6}$$

where ω is the energy of the electron measured from the Fermi surface, v is the velocity of the electron and c is the concentration of impurities.

Substituting the expression for $t(\omega)$ given in (2) into expressions for L_0 and L_1 we have

$$\begin{aligned}L_0&=\frac{N}{m}\int_{-\infty}^{\infty}\frac{d\omega}{4T}\frac{\cosh^{-2}(\omega/2T)}{[-2c\,\mathrm{Im}\,t(\omega)]}\\ &\simeq\frac{N}{m}\left\{\frac{c}{\pi\rho}\left(1-\cos(2\eta)\frac{\tau}{[\tau^2+\pi^2 s(s+1)]^{1/2}}\right)\right\}^{-1}\end{aligned} \tag{7}$$

and

$$L_1 \cong \frac{N}{m}\int_{-\infty}^{\infty}\frac{d\omega}{4T}\frac{\omega\cosh^{-2}(\omega/2T)}{[-2c\,\mathrm{Im}\,t(\omega)]}$$

$$\cong -\frac{N}{m}\sin(2\eta)\left\{\frac{c}{\pi\rho}\left(1-\cos(2\eta)\frac{\tau}{(\tau^2+\pi^2 s(s+1))^{1/2}}\right)\right\}^{-2}$$

$$\times\frac{c}{\pi\rho}\frac{\pi^2 s(+1)}{(\tau^2+\pi^2 s(s+1))^{3/2}}\int_{-\infty}^{\infty}\frac{d\omega}{4T}\omega\,\mathrm{Im}\left\{\psi\left(\frac{1}{2}+\frac{i\omega}{2\pi T}\right)\right\}\cosh^{-2}\left(\frac{\omega}{2T}\right)$$

$$\cong -\frac{cm}{\pi\rho N}L_0{}^2\frac{\pi T}{2}\frac{\pi^2 s(s+1)\sin(2\eta)}{(\tau^2+\pi^2 s(s+1))^{3/2}}, \tag{8}$$

where

$$\tau=\ln\frac{T}{T_K}.$$

Finally we obtain the following expression for the thermoelectric power:

$$\mathfrak{S}=-\frac{\pi}{2e}\frac{\sin(2\eta)}{1-\cos(2\eta)\{\tau/(\tau^2+\pi^2 s(s+1))^{1/2}\}}\frac{\pi^2 s(s+1)}{(\tau^2+\pi^2 s(s+1))^{3/2}}. \tag{9}$$

In the above derivation we neglected completely the effect due to the electron-phonon interaction which may not be negligible if we are concerned with the phenomena at higer temperatures. It may be of some interest to point out that in the present problem, we cannot use the conventional expression for the thermoelectric power:

$$\mathfrak{S}=\frac{\pi^2 T}{3e}\frac{\partial(\ln\sigma(E))}{\partial E}\bigg|_{E=\zeta}, \tag{10}$$

where ζ is the chemical potential.

From (9) we see that the sign of the thermoelectric power depends on η, through the factor $\sin(2\eta)$. This dependence on $\sin(2\eta)$ has been already noted by Fischer,[2] who calculated the thermoelectric power by a perturbational method. In fact in the limit $T\gg T_K$, (9) reduces to the one found by him. Since we can express $\sin(2\eta)$ as

$$\sin(2\eta)=\frac{2\pi\rho V}{1+(\pi\rho V)^2}, \tag{11}$$

we may say that we have a positive thermoelectric power for $V<0$ and a negative one for $V>0$. This criterion has been noted already by Suhl and Wong.[1] The phase shift η may be most conveniently determined form the electrical resistivity. Since the resistivity due to the magnetic impurities is given as[11]

$$R(T)=\frac{mc}{e^2 N\pi\rho}\left(1-\cos(2\eta)\frac{\tau}{(\tau^2+\pi^2 s(s+1))^{1/2}}\right), \tag{12}$$

which reduces to

$$R(0)=\frac{m}{e^2N}\frac{c}{\pi\rho}\cos^2(\eta) \tag{13}$$

at

$$T=0°\mathrm{K}.$$

It is of interest to note that (13) is very similar to the well-known Friedel's result

$$R(0)=\frac{m}{e^2N}\frac{c}{\pi\rho}\sin^2\delta\,, \tag{14}$$

where δ is the phase shift of the electron at the Fermi surface. We may interpret (13) that the existence of the Kondo effect changes the phase shift due to the ordinary potential V by $\pi/2$ at $T=0°\mathrm{K}$.*) Comparing this with Friedel's sum rule, we may speculate that the *s-d* exchange potential removes one of or adds one to electrons trapped by the potential V.

Finally if there exist a number of different impurities in a noble metal, their effects on the thermoelectric power are not additive. However, if we introduce a new quantity $R\mathfrak{S}$ (i.e. the product of the resistivity and the thermoelectric power), we have a simple relation

$$R\mathfrak{S}=\sum_i R_i\mathfrak{S}_i\,, \tag{15}$$

where R_i and $\mathfrak{S}_i$ are corresponding quantities in the presence of only the i-th impurities.

In conclusion I would like to thank Prof. K. Yosida for interesting discussion about the relation between (13) and (14).

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*) A similar relation has been noted previously by Appelbaum and Kondo (J. A. Appelbaum and J. Kondo, Phys. Rev. Letters **19** (1967), 906). However there is an essential difference that they obtained the similar relation independent of sign of J, while the correct theory gives the relation only for negative J (i.e. antiferromagnetic). I am grateful to Dr. Kondo for calling my attention to their work.