IMPURITY MASS DEPENDENCE OF THE THERMOPOWER OF DILUTE ALLOYS AT LOW TEMPERATURES

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If we write down the standart macroscopic transport equations

$$\vec{E} = \rho \vec{j} + Q \nabla T$$
$$\vec{q} = \Pi \vec{j} - \varkappa \nabla T \quad ,$$

then the kinetic coefficient Q is called the absolute differential thermopower and defines all the thermoelectrical properties of a medium. Usually one separates Q in two parts: Q_e - electronic part (sometimes refered to as diffusional one) and Q_{ph} - phonon part due to electron - phonon drag, so that

$$Q = Q_e + Q_{ph} = a \cdot T + b \cdot T^3 \qquad (1)$$

We concentrate our attention on the Q_e which may be written in more convenient form with the use of the dimensionless parametr ξ

$$Q_e = Q_0 \cdot \xi \quad , \quad Q_0 = L_0 e (T/\mathcal{E}_F) \sim 10^{-8} (V/K) \text{ (for typical metals)}, \qquad (2)$$

where Lorenz number is introduced

$$L_0 = \varkappa_e / T\sigma = (\pi^2 k_B^2 / 3e^2) \text{ (for free electrons)}.$$

Now if the scattering processes are elastic, e.g. usual scattering of electrons on impurity atoms, then well known Mott equation is valid

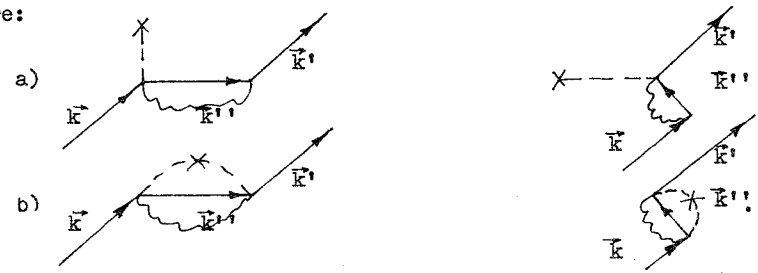
$$\xi = \left[\partial \ln \sigma(\mathcal{E}_{\vec{k}}) / \partial \ln \mathcal{E}_{\vec{k}} \right]_{\mathcal{E}_{\vec{k}} = \mathcal{E}_F} \quad , \qquad (3)$$

where the energy derivative has to be calculated at the Fermi level. The quantity $\sigma(\mathcal{E}_{\vec{k}})$ defines electrical conductivity

$$\sigma = \int d\mathcal{E}_{\vec{k}} \, \sigma(\mathcal{E}_{\vec{k}})$$

and under above condition of elasticity it may be expressed

certain diagrams of the second order of the scattering matrix appear to be important for the thermopower in alloys. Nielsen and Taylor [3] from the U.S. in 1968 realized this fact for the first time. The two important diagrams relevant to alloys are shown here:

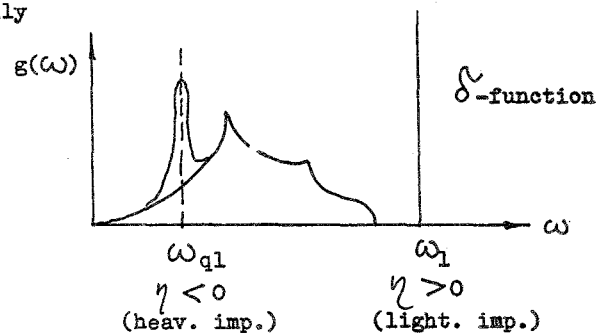


You see that the interference occurs between the two scattering processes mentioned above. You see also both processes are elastic as a whole. Of course the exist of virtual phonon during the scattering strongly decreases the magnitude of the T-matrix corrections proportionally to m/M (electron to ion masses). From the other hand however due to a such phonon the Fermi function of the intermediate state electron doesn't eliminate for both T-matrix corrections $T_a^{(2)}$ and $T_b^{(2)}$. Each of this corrections is the sum of two different scattering processes shown to the left and to the right. In the former case the usual scattering is shown when an electron in the origin $\vec{k}$ - state transfers through the intermediate $\vec{k}''$ - state to the final $\vec{k}'$ - state. In the other processes shown to the right at first the electron-hole pair $(\vec{k}', \vec{k}'')$ creates and then one of the partners of this pair annihilates with the $\vec{k}$ - electron. Because of the Fermi function of the intermediate state electrons the energy derivative of the scattering probability (3), (4) is of anomalous value $\sim (m/M)(\varepsilon_F/\theta)^2 \sim 1$ (θ - Debye temperature).

Thus you see that although electrons scatter mainly on impurities in the case corresponding to our experimental situation ($C_i \lesssim 0{,}2\%$, $T \sim 5K$) the properties of the phonon system play the important role for the case of the thermopower.

As for the phonon system the main effect of introducing impu-

rity atoms into hostal lattice is to vary the caracter of vibrations of the lattice [4] (if of course one considers a substitutional alloy and ignores force constants variations). In the case of lighter impurity atom ($\eta>0$) the so called local mode of vibration occurs in the spectral density of vibrations. In the other case of heavier impurity atom ($\eta<0$) the quasilocal mode may occur. Here frequency distribution function, i.e. g - function is plotted schematically



with the peaks of local and quasilocal modes of vibrations.

This variation in the phonon system immediately results in variations of thermodynamic and kinetic properties of alloy. For the electrical conductivity this effect was taken into account for the first time by Kagan and Zhernov [5]. However unlike these first order calculations in the case of the thermopower it needs to consider the second order corrections. Corresponding calculations are presented below briefly.

If we denote eigenfunctions of the dynamic matrix of the perturbed lattice by $B_s^{\alpha}(\vec{r}_{\vec{n}})$ with $s\equiv(\vec{q},\vec{s})$, then the components of the displacement of the $\vec{n}$ - atom are following (in the second quantized form):

$$u_{\vec{n}}^{\alpha} = \left(\frac{\hbar}{2M_{\vec{n}}}\right)^{1/2} \sum_{s} \frac{B_s^{\alpha}(\vec{r}_{\vec{n}})}{\sqrt{\omega_s}} \left(a_s + a_s^{+} \right)$$

The Green functions should be found from Dyson-like equation in the first order on the impurity concentration. It is rather familiar procedure, e.g. see [4].

After squaring the total amplitude of the T-matrix obtained to the second order and averaging of Green functions over impurity sites we find the scattering probability

$$w_{\vec{k}\vec{k}'} = \frac{2\pi}{\hbar} c_i N \delta(\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'})(P_0 + P_a + P_b)$$

$$P_0 = \left| W_{\vec{k}\vec{k}'} \right|^2 ,$$

$$P_a = 4 \sum_{\vec{k}''} W_{\vec{k}\vec{k}'} V_{\vec{k}'\vec{k}''} W_{\vec{k}''\vec{k}} (\vec{k}'-\vec{k}'')\cdot(\vec{k}''-\vec{k}) \frac{f_{\vec{k}''}}{M} \mathrm{Re}\left[\frac{1}{\tilde{\omega}^2 - \omega^2_{\vec{k}''-\vec{k}}} \cdot \frac{1}{1 - \eta\tilde{\omega}^2 D(\tilde{\omega}^2)} \right] ,$$

$$P_b = 2 \sum_{\vec{k}''} W_{\vec{k}\vec{k}'} W_{\vec{k}'\vec{k}''} W_{\vec{k}''\vec{k}} (\vec{k}'-\vec{k}'')\cdot(\vec{k}''-\vec{k}) \frac{f_{\vec{k}''}}{M} \mathrm{Re}\left[\frac{D(\tilde{\omega}^2)}{1 - \eta\tilde{\omega}^2 D(\tilde{\omega}^2)} \right]$$

where

$$D(\omega^2) = \frac{1}{3N} \sum_{\vec{k},\alpha} \frac{1}{\omega^2 - \omega^2_{\vec{k},\alpha}} , \qquad \tilde{\omega}^2 = \omega^2 + i0 .$$

Bearing in mind the whole elasticity of the processes and using (3),(4) we find the two corrections to the thermopower

$$\Delta\xi_a = -\frac{3\varepsilon_F}{2\pi^2 k_F^4} \frac{mNZ}{M\hbar^2} \int_{-\infty}^{+\infty} \frac{x^2 dx}{(e^x-1)(1-e^{-x})} V \left[\Delta(\omega^2) \int_0^{q_{max}} \frac{q^3 dq}{\omega^2 - \omega_q^2} - \pi\gamma(\omega^2) \int_0^{q_{max}} q^3 dq\, \delta(\omega^2 - \omega_q^2) \right]$$

$$\Delta\xi_b = -\frac{3\varepsilon_F}{\pi^2\hbar^2} \frac{mNZ}{M} \int_{-\infty}^{+\infty} \frac{x^2 dx}{(e^x-1)(1-e^{-x})} W \left[I(\omega^2)\Delta(\omega^2) - \pi g(\omega^2)\gamma(\omega^2) \right]$$

where $x = \hbar\omega / k_B T$ and well known functions from the theory of lattice vibrations are introduced

$$I(\omega^2) = \int_0^{\omega_{max}} \frac{g(\omega_q^2)\, d\omega_q^2}{\omega^2 - \omega_q^2}$$

Now we take the familiar expression for the electron-ion interaction known as the rigid ion approximation

$$H_{int} = \sum_{\vec{n}} V(\vec{r} - \vec{r}_{\vec{n}} - \vec{u}_{\vec{n}}) + \sum_{\vec{n}}{}' W(\vec{r} - \vec{r}_{\vec{n}} - \vec{u}_{\vec{n}}) \quad ,$$

where the second sum is performed only over the impurity sites and $W = U - V$. In the second quantized form we have

$$H_{int} = \sum_{\vec{k},\vec{k}'} c^{+}_{\vec{k}'} c_{\vec{k}} \Big\{ W_{\vec{k}'\vec{k}} \cdot NR(\vec{K}) + iV_{\vec{k}'\vec{k}} \left(\frac{\hbar}{2}\right)^{1/2} \sum_{s} \frac{a_s + a_s^{+}}{\sqrt{\omega_s}} \sum_{\alpha} K^{\alpha} \sum_{\vec{n}} \frac{B_s^{\alpha}(\vec{r}_{\vec{n}})}{\sqrt{M_{\vec{n}}}} \exp(i\vec{K}\vec{r}_{\vec{n}}) + iW_{\vec{k}'\vec{k}} \left(\frac{\hbar}{2}\right)^{1/2} \sum_{s} \frac{a_s + a_s^{+}}{\sqrt{\omega_s}} \sum_{\alpha} K^{\alpha} \sum_{\vec{n}} c_{\vec{n}} \frac{B_s^{\alpha}(\vec{r}_{\vec{n}})}{\sqrt{M_{\vec{n}}}} \exp(i\vec{K}\vec{r}_{\vec{n}}) \Big\},$$

where N is the total number of atoms and

$$NR(\vec{K}) = \sum_{\vec{n}} \exp(i\vec{K}\vec{r}_{\vec{n}})$$

$$\vec{K} = \vec{k} - \vec{k}'$$

$$c_{\vec{n}} = \begin{cases} 1 & \text{for imp. sites} \\ 0 & \text{for hostal sites} \end{cases} .$$

Having this Hamiltonian we get the two second order corrections of the T-matrix mentioned above

$$T^{(2)}_{a\,\vec{k}'\vec{k}} = 2 \sum_{\alpha,\beta} \sum_{\vec{k}''} V_{\vec{k}'\vec{k}''} W_{\vec{k}''\vec{k}} (\vec{k}'-\vec{k}'')_{\alpha} (\vec{k}''-\vec{k})_{\beta} f_{\vec{k}''} \times \sum_{\vec{n},\vec{n}'} c_{\vec{n}'} G^{\alpha\beta}_{\vec{n}\vec{n}'}(\omega^2) \exp\left[i(\vec{k}'-\vec{k}'')\vec{r}_{\vec{n}} + i(\vec{k}''-\vec{k})\vec{r}_{\vec{n}'} \right] ,$$

$$T^{(2)}_{b\,\vec{k}'\vec{k}} = \sum_{\alpha,\beta} \sum_{\vec{k}''} W_{\vec{k}'\vec{k}''} W_{\vec{k}''\vec{k}} (\vec{k}'-\vec{k}'')_{\alpha} (\vec{k}''-\vec{k})_{\beta} f_{\vec{k}''} \times \sum_{\vec{n},\vec{n}'} c_{\vec{n}} c_{\vec{n}'} G^{\alpha\beta}_{\vec{n}\vec{n}'}(\omega^2) \exp\left[i(\vec{k}'-\vec{k}'')\vec{r}_{\vec{n}} + i(\vec{k}''-\vec{k})\vec{r}_{\vec{n}'} \right] ,$$

where $\hbar\omega = \varepsilon_{\vec{k}} - \varepsilon_{\vec{k}''}$, $f_{\vec{k}''}$ - Fermi function of the intermediate state electrons and pair $\vec{k}''$ combinations of the $B_s^{\alpha}(\vec{r}_{\vec{n}})$ - eigenfunctions are substituted by the Green functions of the perturbed lattice

$$G^{\alpha\beta}_{\vec{n}\vec{n}'}(\omega^2) = \frac{1}{\sqrt{M_{\vec{n}} M_{\vec{n}'}}} \sum_{s} \frac{B_s^{\alpha}(\vec{r}_{\vec{n}}) B_s^{\beta}(\vec{r}_{\vec{n}'})}{\omega^2 - \omega_s^2}$$

$$\Delta(\omega^2) = \frac{1 - \eta\omega^2 \cdot I(\omega^2)}{[1 - \eta\omega^2 \cdot I(\omega^2)]^2 + [\pi\eta\omega^2 \cdot g(\omega^2)]^2}$$

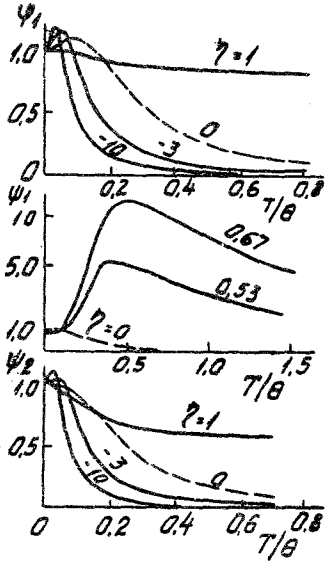
$$\gamma(\omega^2) = \frac{\pi\eta\omega^2 g(\omega^2)}{[1 - \eta\omega^2 \cdot I(\omega^2)]^2 + [\pi\eta\omega^2 \cdot g(\omega^2)]^2} .$$

In this form the results are valid for cubic lattice with an arbitrary spectrum of vibrations and the pseudopotential formfactors are taken to be constants for simplicity. If we accept the Debye model of vibrations the q - integrals considerably simplify and the final formulas acquire the form analogous to the Nielsen and Taylor results but with the other dimensionless functions $\Psi_1(T), \Psi_2(T)$

$$\Delta\xi_a = \frac{\varepsilon_F V}{(k_B\theta)^2} \frac{m}{M} (2/Z)^{1/3} \Psi_1(T/\theta)$$

$$\Delta\xi_b = \frac{\varepsilon_F W}{(k_B\theta)^2} \frac{m}{M} 6Z \Psi_2(T/\theta)$$

We have computed these functions and they are shown here. The dashed lines correspond to $\eta = 0$ and are of Nielsen - Taylor results. You see appreaciable variations in the temperature dependence of these corrections. When $T \to 0$ both $\Psi_1, \Psi_2 \to 1$ for any value of η. At high temperatures $\Psi_1, \Psi_2 \sim 1/T$ except for the case $\eta = 1$ relevant to the scattering of electrons on vacancies. In such a case $\Psi_1 \to 5/6$, $\Psi_2 \to 5/9$. We see that when quasilocal mode occurs ($\eta < 0$) the temperature dependence of the electronic part of the thermopower has low temperature peak, not so high but rather sharp. When local mode arrises the appreaciable hump in Ψ_1 occurs at rather high tempe-



rature. The temperature positions of these humps are $T^{*} \approx \omega_o/3$ where ω_o - the frequency of the local or quasilocal mode.

And finally you may see also that in low temperature region where our experiment were carried out these two functions can be approximated by parabolas. Therefore when experimental results are presented in the form of two parts of the thermopower $Q_e \sim T$ and $Q_{ph} \sim T^3$, the considered effect contributes (and consequently masks) to the phonon drag part of the thermopower but not to the electronic one.

References:

1 N.V.Zavaritsky, A.A.Altukhov, Zh.Ex.T.Ph., 70,1861 (1976)

2 A.A.Altukhov. Yu.K.Dzhikayev, N.V.Zavaritsky, I.M.Suslov, Zh.Ex.-T.Ph., 75, 2256 (1978)

3 P.E.Nielsen, P.L.Taylor, Ph.R.Lett.,21, 893 (1968); Ph.R. B10, 4061 (1974)

4 A.A.Maradudin, E.W.Montroll, G.H.Weiss, I.P.Ipatova, Sol. St. Phys., Acad. Press, N.Y. 1971, Suppl. 3

5 Yu.Kagan, A.P.Zhernov, Zh.Ex.-T.Ph., 50, 1107 (1966)

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