THERMOELECTRIC PROPERTIES OF ULTRADISPERSE MATERIALS

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Formulas for estimating thermoelectric properties in ultradisperse materials are obtained. The possibility of increasing the thermoelectric efficiency is analyzed.

Interest has recently developed in finely granular systems (grain diameter $d < 10$ μm) as a result of the experimental discovery of their unique properties. Thus, it has been shown that in ultradisperse materials the superconducting-state transition temperature is increased, the photoemf rises, and the mechanical properties are improved in comparison with massive (monolithic) samples [1]. It was also established that the thermoelectric efficiency $Z = \alpha^2/\rho\lambda$ of the ultradisperse systems is increased severalfold.

The structure of ultradisperse systems that are free from external compression is of the form in Fig. 1. Here, regions of dense grain packing permeating large cavities (pores) are clearly visible. Therefore, the problem of determining the physical properties of this system divides into two stages: first the properties of the cluster (accumulation) of densely packed particles must be determined, and then the effective properties of the whole system.

The thermal and electrical conductivities of the cluster of densely packed particles are determined on the basis of a notional mean element (Fig. 2) [2].

There is no unanimity yet as to the possible cause of the increase in Z and change in α in an ultradisperse system. Two proposals have been made, as follows.

1) Energy barriers arising in the particle contact region scatter the phonons and weakly influence the electron motion. This leads to an increase of $\beta_{ef} = \sigma_{ef}/\lambda_{ef}$, and hence of Z_{ef} when $\alpha_1 \simeq \alpha_2$.

2) Barriers in the contact region cut off the high-energy electrons, which leads to increase in α_{ef}, and hence in z when $\beta_{ef} \simeq \beta_1$.

These two possibilities will now be analyzed.

Analysis of the thermal and electrical conductivity of a cluster of densely packed particles shows that the basic influence on the properties of the system is exerted by the following parameters: the barrier in the contact region; the properties of the particle itself; and the ratio between the linear dimensions of the barrier and the particles in the direction of the flow (thermal, electrical). For point contact spots between particles, ultradisperse systems may be represented in the form of conducting regions separated by thin dielectric shells. Therefore, below, to analyze the basic physical phenomena in an ultra-

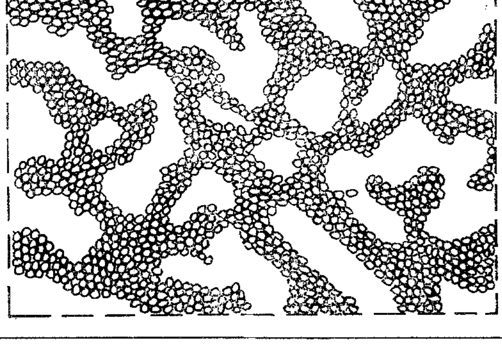

Fig. 1. Structure of ultradisperse system.

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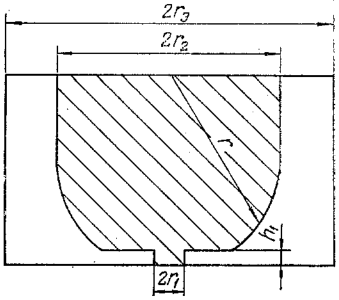

Fig. 2

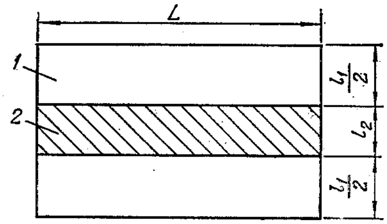

Fig. 3

Fig. 2. Mean element of a cluster of densely packed particles: r, particle radius; r_1, contact-spot radius; $r_2 = 2r\sqrt{n_k - 1}/n_k$; n_k is the mean coordination number; $r_3 = r_2(\sqrt{1 - m_2})$; m_2 is the porosity of the granular system; $(r_3 - r_2)$ is the thickness attributed to the free pore; h_1 is the contact-gap height.

Fig. 3. Laminar system: 1) particle; 2) contact region.

disperse material, a laminar system (Fig. 3) in which the layers are perpendicular to the direction of flow is considered. The first layer has the properties of the particle and the second the properties of the contact region of the particle. So as to be specific, the properties of a vacuum thin slit will be assumed for the second region.

Analysis shows that in ultradisperse systems increase in Z is only possible by over-the-barrier emission. The tunnel effect does not give a contribution to the increase in Z. The electrical conductivity of region 2 due to over-the-barrier emission may be defined in the form

$$\sigma_2 = \frac{CeTl_2}{K} \exp\left(-\frac{U}{KT}\right); \tag{1}$$

where U is the potential-barrier height

$$U = \varphi_0 - \frac{e^2}{\pi\varepsilon_2 l_2}. \tag{2}$$

The thermal conductivity of region 2 is

$$\lambda_2 = \lambda_e + \lambda_r, \tag{3}$$

where $\lambda_e = L_2\sigma_2 T$ is the thermal conductivity due to transport by electrons; L_2, Lorentz number of region 2; $\lambda_r = \sigma_{SB}T^3 l_2$, thermal conductivity due to radiant energy transfer.

The thermal emf coefficient of region 2 is

$$\alpha_2 = 2\,\frac{K}{e}\left(1 + \frac{U}{2KU}\right). \tag{4}$$

The effective electrical resistivity ρ_{ef} and thermal conductivity λ_{ef} of the laminar system are defined as follows

$$\rho_{ef} = \rho_1\bar{l}_1 + \rho_2\bar{l}_2 + \Delta\rho;\ \bar{l}_1 = \frac{l_1}{l_1 + l_2},\ \bar{l}_2 = \frac{\bar{l}_2}{l_1 + l_2}, \tag{5}$$

where $\Delta\rho$ is the additional electrical conductivity due to thermoelectric inhomogeneity [3]:

$$\Delta\rho = \frac{(\alpha_1 - \alpha_2)^2}{\lambda_1\bar{l}_2 + \lambda_2\bar{l}_1}\,\bar{l}_1\bar{l}_2; \tag{6}$$

$$\lambda_{ef} = \lambda_1\left(\frac{\nu_\lambda}{\bar{l}_2 + \nu_\lambda\bar{l}_1}\right);\ \nu_\lambda = \frac{\lambda_2}{\lambda_1}. \tag{7}$$

The thermal emf coefficient is

$$\alpha_{ef} = \alpha_1 \left(\frac{\nu_\lambda \bar{l}_1 + \bar{l}_2 \nu_\alpha}{\bar{l}_2 + \nu_\lambda \bar{l}_1} \right), \quad \nu_\alpha = \frac{\alpha_2}{\alpha_1}. \tag{8}$$

The thermoelectric efficiency of the system is then

$$Z_{ef} = \frac{\alpha_{ef}^2}{\lambda_{ef}\rho_{ef}} = Z_1 \frac{(\bar{l}_1 + \nu_\alpha \nu_\lambda^{-1} \bar{l}_2)^2}{(\bar{l}_1 \nu_\lambda + \bar{l}_2)(\bar{l}_1 + \nu_\rho \bar{l}_2 + \Delta\rho/\rho_1)}. \tag{9}$$

Consider a few cases.

1. Let $\alpha_1 = \alpha_2$, $\lambda_2 \neq \lambda_1$, $\rho_2 \neq \rho_1$. Then Eq. (9) takes the form

$$Z_{ef} = Z_1 \frac{\bar{l}_1 + \nu_\lambda^{-1} \bar{l}_2}{\bar{l}_1 + \nu_\rho \bar{l}_2}. \tag{10}$$

It follows from Eq. (10) that $Z_{ef} > Z_1$ if $\nu_\lambda^{-1} > \nu_\rho$, i.e., that

$$\frac{\lambda_1}{\lambda_2} > \frac{\sigma_1}{\sigma_2}. \tag{11}$$

Taking into account that $\lambda_2 = \sigma_2 L_2 T$ ($\lambda_r \ll \lambda_e$), gives

$$\lambda_1 > L_2 \sigma_1 T, \text{ i.e. } \lambda_1 > \lambda_{1e} \frac{L_2}{L_1}, \tag{12}$$

where L_1 is the Lorentz number for the particles ($\lambda_{1e} = L_1 \sigma_1 T$).

If $L_2/L_1 = 1$, then the condition $Z_{ef} > Z_1$ when $\alpha_1 = \alpha_2$ can be satisfied when the electronic component of the thermoconductivity in the grains is much less than the remaining terms (photonic, excitonic, etc.).

2. Let $\alpha_1 \neq \alpha_2$; $\lambda_2 \approx \lambda_1$. In this case, $Z_{ef} > Z_1$ if

$$(l_1 + \nu_\alpha \bar{l}_2)^2 > \left(\bar{l}_1 + \nu_\rho \bar{l}_2 + \frac{\Delta\rho}{\rho_1} \right). \tag{13}$$

Consider the case of "thin" barriers when $U \ll KT$. In this case $\nu_\rho \gg Z_1 T(1 - \nu_\alpha)^2 \bar{l}_1$, and Eq. (13) may be replaced by the stronger inequality

$$\frac{\alpha_2}{\alpha_1} > \frac{\rho_2}{\rho_1}. \tag{14}$$

Taking Eqs. (1) and (4) and the condition $U \ll KT$ into account, it is found that

$$2CTl_2 > \frac{\alpha_1}{\rho_1}. \tag{15}$$

Thus, increase in $Z_{ef} > Z_1$ in case 2 is possible when Eq. (15) is satisfied.

In terms of individual materials, Eq. (15) is satisfied only for a few elements: Ge, Se, Te.

It should be noted that, with decrease in the grain diameter, the particle properties λ, ρ, and α change on account of the Laplace pressure arising because of the curvature of the particle surface. Thus, for particles with $d \sim 10^{-2}$ μm, the compressive pressure reaches 10^3 atm, which causes a relative decrease in the particle volume by a few percent. At such pressures, the properties of the material may change significantly, and this must be taken into account in estimating Z_{ef}.

The analytical dependences obtained allow purposeful material searches to be conducted in creating high-thermoelectric-efficiency materials on the basis of ultradisperse systems.

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METHOD AND CERTAIN RESULTS OF A SEMIEMPIRICAL DESCRIPTION OF THE HEAT CONDUCTIVITY OF COMPOSITE MATERIALS

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A semiempirical method of describing the heat conductivity of composite materials is described. Examples are presented of its application to determine the heat conductivity of gas mixtures, solid-porous quartz materials, and aluminosilicate refractories.

The expression of the effective transport coefficients of heterogeneous systems in terms of the transport coefficients of the components is the main content of research by a large number of authors to whom references can be found in [1, 2].

Some new results which have successfully been obtained in a consideration of the heat transport in a heterogeneous material from the aspect of one of the known approaches

TABLE 1. Comparison of Results of Computing the Heat Conductivity of Binary Mixtures of Monatomic Gases by the Hirschfelder et al. Method [9] ($\lambda_{[9]}$, W/m·deg) and Formula (4) with the Constant $K_{1.2}$ (λ, W/m·deg)

Mixture composition	Parameter	Volume light gas concentration				
		0,1	0,3	0,5	0,7	0,9
He — Ne	$\lambda_{[9]}$	0,05348	0,06553	0,08181	0,10390	0,13443
	λ	0,05381	0,06600	0,08181	0,10317	0,13357
	$\frac{\lambda_{[9]}-\lambda}{\lambda_{[9]}}\cdot 100\%$	0,620	0,710	0,00	—0,710	—0,640
He — Ar	»	0,02273	0,03533	0,05291	0,07899	0,12137
		0,02277	0,03539	0,05291	0,07883	0,12113
		0,160	0,170	0,00	—0,190	—0,200
He — Kr	»	0,01415	0,02616	0,04330	0,06970	0,11562
		0,01416	0,02617	0,04330	0,06967	0,11558
		0,033	0,033	0	—0,032	—0,032
He — Xe	»	0,00998	0,02061	0,03626	0,06159	0,10953
		0,00998	0,02061	0,03626	0,06155	0,10952
		0,013	0,004	0	—0,009	—0,012
Ne — Ar	»	0,01956	0,02384	0,02904	0,03549	0,04370
		0,01956	0,02384	0,02904	0,03549	0,04370
		0,0057	0,0072	0,00	—0,0075	—0,0071
Ne — Kr	»	0,01115	0,01539	0,02104	0,02891	0,04054
		0,01116	0,01541	0,02104	0,02888	0,04050
		0,094	0,108	0	—0,104	—0,106
Ne — Xe	»	0,00736	0,01116	0,01651	0,02458	0,03801
		0,00737	0,01117	0,01651	0,02453	0,03794
		0,140	0,150	0	—0,170	—0,180
Ar — Kr	»	0,00994	0,01118	0,01265	0,01439	0,01649
		0,00995	0,01119	0,01265	0,01438	0,01647
		0,110	0,130	0	—0,130	—0,110
Ar — Xe	»	0,00642	0,00782	0,00967	0,01213	0,01551
		0,00644	0,00785	0,00967	0,01208	0,01545
		0,330	0,410	0	—0,420	—0,370
Kr — Xe	»	0,00607	0,00660	0,00723	0,00799	0,00889
		0,00608	0,00661	0,00723	0,00798	0,00888
		0,100	0,120	0	—0,120	—0,110

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