

Thermoelectric power of dilute tin-base alloys

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The results are given of measurements of the thermoelectric power of tin alloyed with Zn, Hg, Tl, and Bi (0.01-0.2 wt.%), carried out in the temperature range 3.7-7.2°K. The electron component α_e of the thermoelectric power of these and other alloys of tin with Cd, In, Sb, Te, and Pb [see N. V. Zavaritskii and A. A. Altukhov, *Sov. Phys. JETP* 43, 969 (1976)] is compared with the results of a theoretical calculation. An analysis is made of the transition from α_{e0} (scattering of electrons by phonons in a pure metal) to α_{ei} (elastic scattering by impurities at maximum concentrations of the latter). A quantitative comparison of the dependence of α_{ei} on the valence of the impurities is made, including second-order corrections in perturbation theory of electron scattering by impurities [P. E. Nielsen and P. L. Taylor, *Phys. Rev. Lett.* 21, 893 (1968); *Phys. Rev. B* 10, 4061 (1974)]. The results of calculations are in good agreement with experiment for elements belonging to the tin series. An analysis is made of the influence on α_{ei} of the deformation of the phonon spectrum of the metal, due to the difference between the atomic masses of impurities and the host lattice. This deformation results in considerable anomalies in the temperature dependence of α_{ei} , which is largely due to the presence of local and quasilocal frequencies in the lattice vibration spectrum. A table of parameters is given for reconstructing the energy dependence of the pseudopotentials of several elements.

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1. INTRODUCTION

The absolute thermoelectric power α is the transport coefficient which describes the appearance of an electric field $\mathbf{E}$ in a sample in which a temperature gradient ∇T is established in the absence of the current: $\mathbf{j}=0$. This coefficient occurs in the standard transport equations which have the following form for a crystal of cubic symmetry in the absence of a magnetic field:

$$\mathbf{E}=\rho\mathbf{j}+\alpha\nabla T, \quad \mathbf{Q}=\Pi\mathbf{j}-\kappa\nabla T, \quad \Pi=\alpha T. \quad (1)$$

Experimental measurements give the emf across a sample between whose ends a temperature difference ∇T is established so that

$$\alpha = -\frac{U}{\Delta T} \Big|_{j=0}. \quad (2)$$

In contrast to the resistivity ρ and thermal conductivity κ , much less experimental work has been done on the thermoelectric power because of experimental difficulties (a typical thermoelectric power developed by metals is $\sim 10^{-8}$ V/°K, so that at low temperatures when $\Delta T \sim 10^{-2}$ °K it is necessary to measure very small emf's $U \sim 10^{-12}$ V) and because of problems in the interpretation of the results. In fact, ρ and κ are governed by the density of states, scattering probability, etc. on the Fermi surface, whereas α is governed by the derivatives of these quantities with respect to the energy and, therefore, among the integral transport coefficients the thermoelectric power is one of the most sensitive to the electron structure of a metal and to the nature of quasiparticle scattering.

The use of quantum magnetometers (for example, SQUID's) has simplified greatly the task of accurate measurement of the thermoelectric power of metals at low temperatures. In an earlier paper¹ two of the present authors investigated the influence of a small amount

of impurities (up to 0.2 wt. %) on the thermoelectric power and thermal conductivity of pure tin in the temperature range 3.7-7.2°K. The temperature dependences of the thermoelectric power of all the samples obeyed the law

$$\alpha = aT + bT^2 = \alpha_e + \alpha_{ph}, \quad (3)$$

where the first term α_e is related to the direct action of a temperature gradient on the electron system and the second term α_{ph} to the drag of electrons by the phonon flux created by the temperature gradient. The coefficient a was found to exhibit a dependence on the impurity concentration and at the maximum concentrations it also depended strongly on the impurity valence Z .

The present paper is a continuation of the earlier study.¹ We shall give the results of new measurements of the impurity thermoelectric power α_i of tin alloyed with Hg, Tl, Bi and Zn and, moreover, we shall interpret the dependences of the thermoelectric power on the concentration c , valence Z , and mass M of the impurities. We have been unable to explain the charge dependence of the impurity thermoelectric power $\alpha_i(Z)$ using the static model of impurities. Calculations carried out using the formulas of the exact scattering theory and the Friedel sum rule² give similar results to those obtained by applying the pseudopotential in the Born approximation (see below) and in both cases is a weak dependence on Z . Therefore, we shall consider the influence of the dynamics of impurity atoms. This influence on the electrical conductivity was first studied by Kagan and Zhernov.³ They found that even in the Born approximation an allowance for the inelastic nature of the scattering of quasiparticles by impurities (i.e., if the scattering is accompanied by the emission or absorption of a phonon) and for the deformation of the lattice vibration spectrum associated with the difference between the masses of the impurity and lattice atoms

has the result that the scattering by impurities and phonons are interdependent processes. This results in a deviation from the Matthiessen rule for the electrical resistivity:

$$\rho = \rho_0 + \rho_i + \Delta\rho(T, c). \quad (4)$$

In the case of the thermoelectric power these corrections are small (at low temperatures) because of two small factors: one of them represents the impurity concentration and the other is of the order of $c(T/\Theta)^n$ and represents temperature (here, Θ is the Debye temperature and the different values of n represent different contributions).

Nielsen and Taylor⁴ considered the problem of the scattering of quasiparticles by impurities in the second order of perturbation theory. They found that if a virtual phonon (see Fig. 4 below) participates in the intermediate state, so that the scattering as a whole is elastic, the corrections to the impurity part of the thermoelectric power are considerable: they are of the same order of magnitude as the thermoelectric power representing the scattering by static impurities. In view of the good agreement between the calculations of Nielsen and Taylor and the experimental data for alkali metals, we shall apply their approach to the charge dependence of the impurity thermoelectric power in our case.

Following Nielsen and Taylor, we shall apply the Heine-Animalu-Abarenkov pseudopotentials⁵ to the lattice and impurity atoms, but (in contrast to Nielsen and Taylor) we shall allow for the dependence of the Fourier components of the pseudopotentials on the transferred momentum $V(q)$.¹¹ Moreover, since Nielsen and Taylor⁴ ignore a possible influence of the difference between the host and impurity atomic masses, we shall analyze the dependence $\alpha_{ei}(M)$.

In calculations of the scattering probability we shall assume that the Fermi surface is isotropic. The corrections to the scattering probability associated with the anisotropy of this surface are in any case small because of the smallness of the pseudopotential itself compared with the characteristic energy of quasiparticles $\sim V/\mu$ (where $\mu = \epsilon_F$ —see Ref. 6), and we shall not consider them here. The topology of the Fermi surface of tin⁷ should affect mainly the low-temperature limit of a pure metal whose thermoelectric power is practically independent of the scattering properties and is governed by the derivative^{8,9}

$$\xi \sim \left. \frac{\partial \ln(vS)}{\partial \ln \epsilon} \right|_{\epsilon = \epsilon_F} \quad (5)$$

where v is the velocity of quasiparticles on a given constant-energy surface and S is the area of this surface. In the impurity limit (i.e., in the case of the maximum impurity concentrations) the thermoelectric power also contains this term but it does not affect the charge dependence (a change in this term results in a simultaneous shift of all the values of the thermoelectric power by a constant amount). Since the experimental data on the low-temperature thermoelectric power of pure tin are not absolutely reliable²¹ we shall replace the Fermi surface of tin with a sphere of radius $k_F(\text{Sn})$.

2. MEASUREMENT METHOD. EXPERIMENTAL RESULTS

The absolute thermoelectric power of tin was measured. The voltage drop which appeared in the sample-superconductor circuit in the presence of a temperature gradient along the sample was compensated in the same way as in Ref. 1. The majority of the measurements were carried out in an inverted Dewar and some complications were encountered in the measurement of ΔT . The maximum error in ΔT could reach 10%. More accurate values of the thermoelectric power and thermal conductivity, and a check of the earlier data, were carried out in a vacuum system (Fig. 1).

In comparison with the conventional apparatus for the thermal conductivity measurements, a distinguishing feature of the vacuum system was that a sample 6 was insulated electrically from heaters H1 and H2, thermometers T1 and T2, and casing 4. A superconductor circuit 2, used to measure the thermoelectric power, was also insulated electrically from the casing. The insulation was provided by glass-ferrochrome seals 3. Thermal contact between the thermometers T1 and T2 and the sample was improved by sealing them in apertures by a spark treatment. The apertures were filled with GZh 94 silicone oil. A support rod 8 carried a carbon thermometer T3, which gave the temperature rise from which the pressure in the system was estimated. The system was evacuated by a backing pump through a German-silver capillary 1 at room temperature and was tightly sealed. Activated carbon 9 established hard vacuum inside the system after cooling. Single-crystal samples were grown in glass molds with a thin coating of soot. The central (investigated) part of a sample, 2 mm in diameter and 30–50 mm long, remained inside the glass mold 5. At the edges glass was etched away and heaters H1 and H2, thermometers T1 and T2, and potential 2 and current 7 terminals were mounted.

Some control samples were freed of the glass mold. Potential lead wires were usually soldered to a sample by Wood's alloy and in some cases these wires were

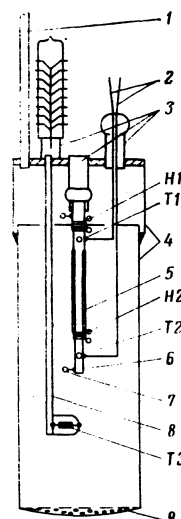


FIG. 1. Schematic diagram of the vacuum system.

3. DEPENDENCE OF THE THERMOELECTRIC POWER ON THE IMPURITY CONCENTRATION

We shall use the variational method of solving the Boltzmann transport equation to explain the impurity-concentration dependence of the thermoelectric power and we shall show that even a very small number of test functions is sufficient to explain qualitatively the change in the thermoelectric power on increase in the impurity concentration. We shall consider only the electron component of the thermoelectric power α_e , because the experimental data on the impurity-concentration dependences of the phonon component α_{ph} are still insufficient for a reliable comparison with the results of a theoretical analysis.

Using the standard test functions

$$\varphi_1 = k_x, \quad \varphi_2 = (e_k - \mu) k_x, \quad \varphi_L = q_x, \quad (7)$$

where $\varphi_{1,2}$ are the electron functions (describing the transport of charge and energy), φ_L is the phonon function, $\mathbf{k}$ and $\mathbf{q}$ are the electron and phonon quasimomenta, $\varepsilon_k = \hbar^2 k^2 / 2m$, and the x axis is selected along the direction of $\mathbf{E}$ and ∇T , we obtain the following expression for the thermoelectric power of a metal⁸:

$$\alpha = \frac{\pi^2 k_B^2 T}{3e\mu} \left\{ \frac{\partial \ln(kS_k)}{\partial \ln \varepsilon_k} \left[1 - \frac{L}{L_0} (1 + \eta_1 - 2\eta_2) \right] + \frac{L}{L_0} \frac{\partial \ln \sigma(\varepsilon_k)}{\partial \ln \varepsilon_k} (1 - \eta_2) - \mu \frac{P_{12}}{P_{11}} (1 - \eta_2) \right\}_{\varepsilon_k = \mu} + \frac{k_B}{e} \frac{4\pi^4}{5Z_0} \left(\frac{T}{\Theta} \right)^3 \left(- \frac{P_{1L}}{P_{LL}} \right), \quad (8)$$

$$\eta_1 = \frac{P_{1L}}{P_{11}P_{LL}}, \quad \eta_2 = \frac{P_{1L}P_{2L}}{P_{11}P_{LL}}.$$

Here, P_{ij} are the standard variational integrals of the $\langle \varphi_i, P \varphi_j \rangle$ type, where P is the collision operator, S_k is the area of the constant-energy surface, $L_0 = \pi^2 k_B^2 / 3e^2$ is the Lorenz number, $L \equiv \nu / \sigma T$ is the Wiedemann-Franz ratio, $\sigma(\varepsilon_k)$ is the "spectral" density of the conductivity [$\sigma \equiv \int \sigma(\varepsilon_k) d\varepsilon_k$], Z_0 is the valence of the solvent metal, and all the quantities are taken at $\varepsilon_k = \mu$. The term in the braces and the last term in Eq. (8) represent, respectively, the electron α_e and phonon α_{ph} components of the thermoelectric power. In the lowest approximation we have $\alpha_e \propto T/\mu$, $\alpha_{ph} \propto (T/\Theta)^3$. It should be noted that P_{1L} and P_{2L} contain only the probability of the electron-phonon scattering, because P_{11} , P_{12} , and P_{22} (P_{LL}) are the probabilities of electron (phonon) scattering by all possible sources; the integral $\tilde{P}_{12}$ describes only the inelastic scattering associated with umklapp processes.

If the impurity concentration is sufficiently high or the temperature is sufficiently low so that $\rho_i \gg \rho_0$, which we shall call the impurity limit, the main contribution to the scattering is due to elastic processes and the Wiedemann-Franz law is satisfied: $L/L_0 = 1$, $\tilde{P}_{12} = 0$, and $\eta_{1,2} \ll 1$. In this case, Eq. (8) becomes identical with the well-known Mott formula

$$\alpha_{ei} = \frac{\pi^2 k_B^2 T}{3e\mu} \frac{\partial \ln \sigma(\varepsilon_k)}{\partial \ln \varepsilon_k} \Big|_{\varepsilon_k = \mu}, \quad (9)$$

which can also be easily obtained in the τ approximation, valid in this case.

On the other hand, for a pure metal with $T \ll \Theta$, we have $L/L_0 \propto (T/\Theta)^2$, which gives

$$\alpha_{e0} = \frac{\pi^2 k_B^2 T}{3e\mu} \left[\frac{\partial \ln(kS_k)}{\partial \ln \varepsilon_k} - \mu \frac{P_{12}}{P_{11}} (1 - \eta_2) \right]_{\varepsilon_k = \mu}. \quad (10)$$

If only the normal scattering processes are allowed for, it is found that $\eta_2 = 1$ and only the first term remains in Eq. (10), i.e., the usual Wilson result^{11,8} is obtained. The occurrence of the umklapp processes results in a deviation from the linear temperature dependence of α_e for a pure metal at low temperatures and this may explain deviations from the linear dependence observed for pure samples.

Introduction of an impurity alters the thermoelectric power α_e (which then varies with the impurity concentration as a power law with a fractional exponent) from the value α_{e0} given by Eq. (10) in the $c=0$ case to the value α_{ei} of Eq. (9) for $\rho_i \gg \rho_0$, which is no longer concentration-dependent. This is in qualitative agreement with the experimental results (see Fig. 6 in Ref. 1). The application of the Gorter formula¹²

$$\alpha_e = \frac{\rho_i}{\rho_i + \rho_0} \alpha_{ei} + \frac{\rho_0}{\rho_i + \rho_0} \alpha_{e0},$$

which is obtained by substituting the Matthiessen rule $\rho = \rho_i + \rho_0$, in Eq. (9), to the impurity-concentration dependence may be justified only if the electron scattering processes are elastic and independent.

4. DEPENDENCE OF THE THERMOELECTRIC POWER ON THE IMPURITY VALENCE

We shall now consider the electron component α_{ei} in the impurity limit (i.e., at the maximum impurity concentrations). In this limit, quasiparticles are scattered mainly by impurities and α_{ei} can be calculated from Eq. (9) using $\sigma(\varepsilon_k)$ in the τ approximation:

$$\sigma(\varepsilon_k) = \frac{e^2}{4\pi^2 \hbar} \tau(\varepsilon_k) v(\varepsilon_k) S_k \quad (11)$$

It is convenient to express α_{ei} in terms of the dimensionless quantity ξ :

$$\alpha_{ei} = \frac{\pi^2 k_B^2 T}{3e\mu} \xi. \quad (12)$$

Next, substituting Eq. (11) into Eq. (9), we obtain

$$\xi = \left\{ \frac{\partial \ln[v(\varepsilon_k) S_k]}{\partial \ln \varepsilon_k} - \frac{\partial \ln[1/\tau(\varepsilon_k)]}{\partial \ln \varepsilon_k} \right\}_{\varepsilon_k = \mu}. \quad (13)$$

If we know the impurity potential, we can find $\tau(\varepsilon_k)$ applying the usual rules of perturbation theory. We shall describe impurities by a pseudopotential W which can be calculated as described in the Appendix. In the Born approximation for the scattering probability, we obtain

$$\frac{1}{\tau(\varepsilon_k)} = \frac{cN}{4\pi\Omega k_F^2} \int_0^{2k_F} |\langle \mathbf{k} + \mathbf{q} | W | \mathbf{k} \rangle|^2 q^2 dq, \quad (14)$$

where $\hbar k_F$ is the Fermi momentum of tin, $\hbar \mathbf{q}$ is the transferred momentum, N and Ω are the number of atoms and the volume of the crystal, respectively. Values of ξ calculated by means of Eq. (14) are listed

calculated results). Integrating with respect to the angles and introducing dimensionless variables, we can easily obtain the following formulas for low temperatures ($T \rightarrow 0$):

$$\left. \begin{aligned} \Delta \xi_a &= \left(\frac{\mu}{k_B \Theta} \right)^2 \frac{m}{M} \left(\frac{2}{Z_0} \right)^{1/2} \frac{\overline{W W V_0}}{\overline{W^2 \mu}} \\ \Delta \xi_c &= \left(\frac{\mu}{k_B \Theta} \right)^2 \frac{m}{M} 6 Z_0 \frac{\overline{W W W}}{\overline{W^2 \mu}} \end{aligned} \right\} \quad (16)$$

Here,

$$\begin{aligned} \overline{W^2} &= 4 \int_0^1 W^2(x) x^3 dx, \\ \overline{W W V_0} &= \frac{12}{\pi} \left(\frac{2k_F}{q_0} \right)^2 \int_0^1 W(x) x^3 dx \int_0^1 V_0(y) dy \\ &\times \int_0^{2\pi} d\varphi [y(1-x^2) - x(1-x^2)^{1/2}(1-y^2)^{1/2} \cos \varphi] W[\gamma(x, y, \varphi)], \\ \overline{W W W} &= \frac{24}{\pi} \int_0^1 W(x) x^3 dx \int_0^1 W(y) y^2 dy \\ &\times \int_0^{2\pi} d\varphi [y(1-x^2) - x(1-x^2)^{1/2}(1-y^2)^{1/2} \cos \varphi] W[\gamma(x, y, \varphi)], \\ \gamma(x, y, \varphi) &= [x^2 + y^2 - 2x^2 y^2 - 2xy(1-x^2)^{1/2}(1-y^2)^{1/2} \cos \varphi]^{1/2}. \end{aligned}$$

The results of a numerical calculation carried out using these formulas are presented in Fig. 3 and in Table I. We can see that in the case of the tin series the quantitative agreement with the experiments is satisfactory. However, there is no agreement in the case of the lead series. An attempt to allow for the influence of the deformation of the lattice vibration spectrum on introduction of impurities with a very different atomic mass (see below) fails to correct the situation. In the limit $T \rightarrow 0$ the difference between masses of the impurity and host atoms should not affect the impurity component of the thermoelectric power. It is possible that the absence of agreement is associated with the neglect of the electron-phonon umklapp processes which are not "frozen out" at low temperatures because phonons participating in the scattering are not thermal. A more likely reason for the disagreement is the lower accuracy of the calculations of the impurity pseudopotentials for elements belonging to a different series of the periodic table. This is confirmed by the fact that similar results are obtained on comparison with the experimental data on the residual resistivity.¹⁰ Although a calculation of ρ_i using the pseudopotential gives a better agreement with the experimental data than the Friedel calculation, the agreement with experiment for the lead series is considerably poorer than for the tin series (Table I).

5. DEPENDENCE OF THE THERMOELECTRIC POWER ON THE IMPURITY MASS

Introduction of an impurity into a metal alters considerably the nature of the lattice vibrations.¹³⁻¹⁵ The thermodynamic¹⁶ and kinetic properties of a metal are affected. In the case of the electrical conductivity, this problem has been investigated in detail by Kagan and Zhernov.³ The question of the influence of the deforma-

tion of the lattice vibration spectrum due to the difference between the masses of the impurity and host atoms on the thermoelectric power of a metal has not yet been considered. We shall report calculations only for the impurity component of the thermoelectric power and consider elsewhere the influence of the mass difference on that part of the thermoelectric power which is associated with the electron-phonon scattering, in particular, with the drag of electrons by phonons.

It should be pointed out that the results for the electrical conductivity obtained in Ref. 3 by a method based on reduction of the scattering probability to the Van Hove correlation function¹⁷ cannot be applied directly to calculations of the thermoelectric power because this approach is restricted significantly by the Born approximation. On the other hand, as pointed out above, it is necessary to allow for the scattering processes in the second order of perturbation theory. We shall use the well-known T matrix method¹⁸ and go over to the Green functions of a vibrating lattice, bypassing the correlation functions.

Let us assume that a lattice composed of atoms of mass M_0 is perturbed by impurities of mass $M = M_0 \times (1 - \varepsilon)$ and that the impurity concentration c is low. The change in the force constants will be ignored. If $B_s^\alpha(\mathbf{r}_n)$ are the eigenfunctions of the dynamic matrix, where $s = (\mathbf{q}, s)$, the displacements of ions can be described by second-quantization operators as follows¹⁵:

$$u_n^\alpha = \left(\frac{\hbar}{2M_n} \right)^{1/2} \sum_s \frac{B_s^\alpha(\mathbf{r}_n)}{\omega_s} (a_s + a_s^\dagger). \quad (17)$$

In this case the Hamiltonian of the interaction of electrons with ions without allowance for two-phonon processes becomes

$$\begin{aligned} H_{int} &= \sum_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \left\{ W_{\mathbf{k}, \mathbf{k}} NR(\mathbf{K}) + V_{0\mathbf{k}, \mathbf{k}} i \left(\frac{\hbar}{2} \right)^{1/2} \sum_s \frac{a_s + a_s^\dagger}{\omega_s^{1/2}} \right. \\ &\times \sum_{\alpha} K^\alpha \sum_n \frac{B_s^\alpha(\mathbf{r}_n)}{M_n^{1/2}} \exp(i\mathbf{K}\mathbf{r}_n) + W_{\mathbf{k}, \mathbf{k}} i \left(\frac{\hbar}{2} \right)^{1/2} \sum_s \frac{a_s + a_s^\dagger}{\omega_s^{1/2}} \sum_{\alpha} K^\alpha \\ &\left. \times \sum_n c_n \frac{B_s^\alpha(\mathbf{r}_n)}{M_n^{1/2}} \exp(i\mathbf{K}\mathbf{r}_n) \right\}, \end{aligned} \quad (18)$$

where $c_{\mathbf{k}}$ and $c_{\mathbf{k}}^\dagger$ are the electron annihilation and creation operators; $W_{\mathbf{k}, \mathbf{k}}$ is the Fourier component of the difference between the pseudopotentials of the impurity V_i and of the host lattice V_0 (normalized to the volume of the crystal); c_n assumes the value 1 for the impurity sites and the value 0 for the others sites; $NR(\mathbf{K}) = \sum_n \exp(i\mathbf{K}\mathbf{r}_n)$ (N is the number of ions in the crystal). The Hamiltonian (18) is equivalent to that used by Kagan and Zhernov³ and a calculation of the transition probability in the first order of perturbation theory gives all the contributions to the electrical conductivity found by them.

If electrons are scattered mainly by impurities, the scattering probability $w_{\mathbf{k}, \mathbf{k}}$ can be calculated ignoring the square of the second term in Eq. (18) (which gives rise to the Bloch resistivity $\rho_0 \ll \rho_i$) and also dropping the first-order corrections to the probability of electron scattering by impurities w_{g-i} .³ Calculation of the contributions of the diagrams in Figs. 4b and 4c to the

transition amplitude gives

$$T_{k'k}^{(0)} = 2 \sum_{\alpha, \beta} \sum_{k''} V_{0k'k''} W_{k''k} (k' - k'')_{\alpha} (k'' - k)_{\beta} f_{k''} \quad (19a)$$

$$\sum_{\alpha, \beta} c_{\alpha} G_{\alpha\alpha}^{\alpha\beta}(\omega^2) \exp[i(k' - k'')r_{\alpha} + i(k'' - k)r_{\beta}],$$

$$T_{k'k}^{(0)} = \sum_{\alpha, \beta} \sum_{k''} W_{k'k''} W_{k''k} (k' - k'')_{\alpha} \quad (19b)$$

$$(k'' - k)_{\beta} f_{k''} \sum_{\alpha, \beta} c_{\alpha} c_{\beta} G_{\alpha\alpha}^{\alpha\beta}(\omega^2) \exp[i(k' - k'')r_{\alpha} + i(k'' - k)r_{\beta}],$$

where $\hbar\omega = \varepsilon_k - \varepsilon_{k''}$.

The pair combinations of functions $B_s^{\alpha}(r_n)$ in Eqs. (19a) and (19b) are then replaced by the Green functions of the perturbed lattice¹⁵

$$G_{\alpha\alpha}^{\alpha\beta}(\omega^2) = \left(\frac{1}{M_n M_{n'}} \right)^{1/2} \sum_i \frac{B_i^{\alpha}(r_n) B_i^{\beta}(r_{n'})}{\omega^2 - \omega_i^2} \quad (20)$$

The Green functions themselves are obtained from the Dyson equation in the first order with respect to the impurity concentration.

Going over to the scattering probability and averaging the Green functions over the impurity positions,¹⁵ we obtain

$$w_{kk'} = 2\pi\hbar^{-1} c N \delta(\varepsilon_k - \varepsilon_{k'}) (P_0 + P_A + P_B) \quad (21)$$

Here,

$$P_0 = |W_{k'k}|^2,$$

$$P_A = 4 \sum_{k''} W_{kk'} V_{0k'k''} W_{k''k} (k' - k'') \times \frac{f_{k''}}{M_0} \operatorname{Re} \left(\frac{1}{\bar{\omega}^2 - \omega_{k''-k}^2} \frac{1}{1 - \varepsilon \bar{\omega}^2 D(\bar{\omega}^2)} \right),$$

$$P_B = 2 \sum_{k''} W_{kk'} W_{k'k''} W_{k''k} (k' - k'') \times (k'' - k) \frac{f_{k''}}{M_0} \operatorname{Re} \frac{D(\bar{\omega}^2)}{1 - \varepsilon \bar{\omega}^2 D(\bar{\omega}^2)},$$

where

$$D(\omega^2) = \frac{1}{3N} \sum_{k, \alpha} \frac{1}{\omega^2 - \omega_{k, \alpha}^2}, \quad \bar{\omega}^2 = \omega^2 + i0.$$

In the case of electron scattering by impurities the thermoelectric power is calculated from Eq. (13). The result is

$$\Delta \xi_B = - \frac{3\mu}{2\pi^2 k_F^4} \frac{m}{M_0 \hbar^2} N Z_0 \int_{-\infty}^{+\infty} \frac{x^2 dx}{(e^x - 1)(1 - e^{-x})} \times V_0 \left[\Delta(\omega^2) \int_0^{q_{\max}} \frac{q^2 dq}{\omega^2 - \omega_q^2} - \pi \gamma(\omega^2) \int_0^{q_{\max}} q^2 dq \delta(\omega^2 - \omega_q^2) \right], \quad (22)$$

$$\Delta \xi_s = - \frac{3\mu}{\pi^2 \hbar^2} \frac{m}{M_0} N Z_0 \int_{-\infty}^{+\infty} \frac{x^2 dx}{(e^x - 1)(1 - e^{-x})} W [J(\omega^2) \Delta(\omega^2) - \pi g(\omega^2) \gamma(\omega^2)],$$

where $x = \hbar\omega/k_B T$; the above expression contains functions familiar from the lattice vibration theory: $g(\omega^2)$ is the distribution of the squares of the frequencies of the unperturbed lattice,

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

$$\Delta(\omega^2) = \frac{1 - \varepsilon \omega^2 J(\omega^2)}{[1 - \varepsilon \omega^2 J(\omega^2)]^2 + [\pi \varepsilon \omega^2 g(\omega^2)]^2}$$

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

The results obtained in this form apply to a cubic lattice with an arbitrary vibration spectrum. In the Debye model the integrals with respect to dq in Eq. (22) simplify and the corrections to the thermoelectric power ξ_0 corresponding to the scattering by static impurities can be described in the same way as in Eq. (15) but using different functions Ψ_2 and Ψ_3 .

The functions Ψ_2 and Ψ_3 found by numerical calculation are shown in Fig. 6. The dashed curves are the results of Nielsen and Taylor obtained without allowance for the mass difference, i.e., for $\varepsilon = 0$ [in this case we have $\Delta(\omega^2) = 1, \gamma(\omega^2) = 0$]. The change in the temperature dependence of the thermoelectric power is large. In the limit $T \rightarrow 0$ the functions become $\Psi_2, \Psi_3 \rightarrow 1$ for any value of ε . For high values T in the case $\varepsilon \neq 1$ we have $\Psi_2, \Psi_3 \propto 1/T$, but if $\varepsilon = 1$ (which corresponds to the scattering by vacancies), then $\Psi_2 \rightarrow \frac{5}{8}, \Psi_3 \rightarrow \frac{5}{8}$. The magnitude of the effect is closely related to the presence of local and quasilocal frequencies. A quasilocal frequency, which appears as usual in the case of very heavy impurity atoms ($\varepsilon < 0$, Ref. 14), gives rise to low-temperature peaks in the thermoelectric power which are not very large but fairly sharp. Introduction of sufficiently light impurities can give rise to a local frequency,¹³ which increases very greatly the value of Ψ_2 at relatively high temperatures. The characteristic temperature of the thermoelectric power maxima is $T^* \approx \omega_0/3$, where ω_0 is the frequency of a local or quasilocal level.¹⁵

The electrical conductivity exhibits similar behavior but in the latter case the effects are small because of the low concentrations. In the case of the thermoelectric power, logarithmic differentiation of the reciprocal of the relaxation time $1/\tau$ with respect to the energy

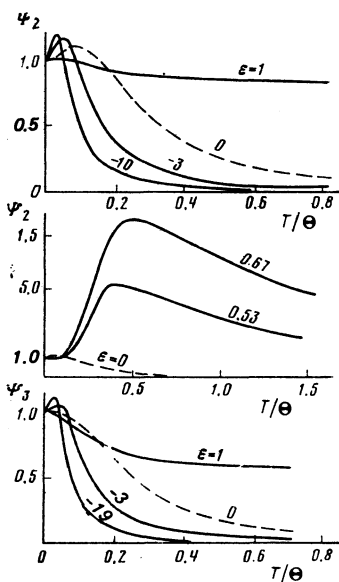


FIG. 6. Dependences of the thermoelectric power on the impurity mass. The value of ε is given alongside each curve.

ensures that the corrections do not contain the impurity concentration and the effects are considerably greater. Nevertheless, experimental detection and investigation of the effects of the deformation of the lattice vibration spectrum due to introduction of impurities with a very different mass meets with considerable difficulties in the case of the thermoelectric power. The main is the separation of the impurity α_i and phonon α_{ph} components, which is not a simple task because of the complex temperature dependences of the two contributions. At very low temperatures ($T \rightarrow 0$) the problem simplifies. Since in narrow intervals near $T=0$ the functions Ψ_2 and Ψ_3 can be approximated by the parabolas

$$\Delta \xi_B = \Delta \xi_B^0 + \xi_B' T^2,$$

$$\Delta \xi_C = \Delta \xi_C^0 + \xi_C' T^2,$$

and the phonon drag gives rise to a cubic temperature dependence $\alpha_{ph} = bT^3$, the value of α/α_0 , where $\alpha_0 = \pi^2 k_B^2 T / 3e\mu$, is a linear function of the square of temperature:

$$\begin{aligned} \alpha/\alpha_0 &= \xi_0 + \Delta \xi_B^0 + \Delta \xi_C^0 \\ &+ (\xi_B' + \xi_C' + b/\alpha_0) T^2. \end{aligned} \quad (23)$$

The experimental values α_{exp} fit well the straight line $\alpha_{exp}/\alpha_0 = \xi_{exp} + b_{exp} T^2/\alpha_0$. However, the much higher values of ξ_{exp} for the heavy impurities (Hg, Tl; $\varepsilon \approx -1$) compared with ξ_{exp} for the impurities with the same valences (Cd, In) but with practically the same mass as tin cannot be explained by the deformation of the lattice vibration spectrum, as can be deduced from Eq. (23). Nevertheless, the phonon drag coefficient b may be masked by the impurity contribution $\xi_B' + \xi_C'$.

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APPENDIX

To calculate α_{ei} , we have to know the pseudopotentials W of impurity atoms in the tin lattice. However, they cannot be determined accurately on the basis of tabulated data because these data do not reflect the energy dependence of the pseudopotential.

We shall use the Heine-Animalu-Abarenkov method⁵ in which the potential of an isolated ion is replaced by the model potential of the type (Fig. 7):

$$V_E(r) = \begin{cases} -Z/r & r \geq R_M \\ -\sum_i A_i(E) P_i & r < R_M \end{cases}, \quad (A.1)$$

where P_l is the operator of the projection on the l -th spherical harmonic. The value of R_M is taken to be of the order of the ionic core radius and the constants A_l are adjusted so that the lower level of the potential (A.1) coincides with the energy of the spectral term $E_{n,l}$ for each value of n in turn. The eigenfunctions of the potential (A.1) in the $r \geq R_M$ case are automatically identical with the true wave functions (since the solu-

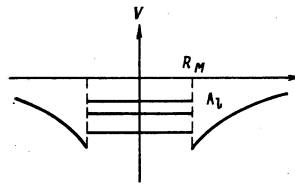


FIG. 7. Coordinate dependence of the model pseudopotential.

tion in the Coulomb field is specified unambiguously by selecting E and by the condition of fall of the radial wave function $R_{nl} \rightarrow 0$ in the limit $r \rightarrow \infty$). For convenience, it is assumed that $A_l = A_2$ for $l > 2$.

When the potential $V_E(r)$ has been constructed, the unscreened form factor can be found:

$$\langle \mathbf{k} + \mathbf{q} | V | \mathbf{k} \rangle = \frac{N}{\Omega} \int e^{-i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r}} V_E(r) e^{i\mathbf{k} \cdot \mathbf{r}} d^3r = V_{\mathbf{k} + \mathbf{q}, \mathbf{k}}. \quad (A.2)$$

For the scattering by a constant-energy surface $|\mathbf{k} + \mathbf{q}| = |\mathbf{k}| = k = (2E)^{1/2}$ (in atomic units) in an isotropic case, we have

$$V_{\mathbf{k} + \mathbf{q}, \mathbf{k}} = V_E(q), \quad q = |\mathbf{q}| \quad (A.3)$$

The nonlocal nature of the pseudopotential appears in this case as an additional energy dependence $V_E(q)$. The screening of the nonlocal potential is allowed for by introducing the screening part⁶

$$\left. \begin{aligned} V_{scr} &= V_E(q) + \Delta V(q), \\ \Delta V(q) &= -\frac{4}{\pi^2 q^2 \varepsilon(q)} \int_{\mathbf{k} < k_F} \frac{V_{\mathbf{k} + \mathbf{q}, \mathbf{k}}}{k^2 - |\mathbf{k} + \mathbf{q}|^2} d^3k. \end{aligned} \right\} \quad (A.4)$$

where

$$\varepsilon(q) = 1 + \frac{4k_F}{\pi q^2} \left(1 + \frac{4k_F^2 - q^2}{8qk_F} \ln \left| \frac{2k_F - q}{2k_F + q} \right| \right).$$

The forms factors $V_E(q)$ (which are now screened) found in this way for the Fermi energy $E = \varepsilon_F$ are given in Ref. 6 for 25 elements.

However, we need the impurity pseudopotentials and, therefore, the unscreened form factor should be taken at $E = \varepsilon_F(\text{Sn})$ and in the screening case one has to use the permittivity $\varepsilon(q)$ of the electron gas in tin [i.e., $k_F = k_F(\text{Sn})$ has to be substituted in Eq. (A.4)]. Finally, the required impurity pseudopotential W is found by subtracting the impurity atom potential V_i calculated as above and the pseudopotential of pure tin V_0 : $W = V_i - V_0$.

It should be noted that the impurity pseudopotentials have the correct limit for $q \rightarrow 0$ and this limit is $-\frac{2}{3}\varepsilon_F \Delta Z / Z_0$, where $\Delta Z = Z - Z_0$, required to satisfy the Friedel sum rule. We can demonstrate this easily by means of the relationship

$$\frac{2}{\pi} \sum_l (2l+1) \delta_l = -\frac{k_F \Omega}{\pi^2 N} W(0),$$

readily obtained from the expressions for the Born phase shifts (see, for example, Ref. 19).

We repeated the above procedure. At the same time we allowed for later comments in Ref. 20, referring to the difference between the true wave functions and the pseudowave functions inside the ion core (depletion hole). The energy dependence of the pseudopotential

Table II.

	A_0	A_1	A_2	R_M	B_0	B_1	B_2	Z	k_F
Cd	0.88	0.98	1.11	2.6	-0.392	-0.194	-1.000	2	0.7423
In	1.32	1.46	1.10	2.4	-0.456	-0.207	-0.020	3	0.7972
Sn	1.84	2.04	1.62	2.0	-0.520	-0.261	-0.177	4	0.8674
Sb	2.42	2.66	2.21	2.0	-0.450	-0.052	0.325	5	0.8986
Te	3.04	3.32	2.80	2.0	-0.432	0.080	0.585	6	0.9209
Hg	0.97	1.11	0.85	2.6	-0.416	-0.490	-0.592	2	0.7213
Tl	1.44	1.51	0.98	2.4	-0.543	-0.333	-0.267	3	0.7738
Pb	1.92	2.03	0.90	2.1	-0.580	-0.352	0.115	4	0.8350
Bi	2.38	2.58	0.25	2.0	-0.545	-0.600	0.260	5	0.8520
Zn	0.99	1.14	0.98	2.2	-0.338	-0.092	-0.193	2	0.8342
Na	0.305	0.339	0.402	3.4	-0.249	-0.065	-0.165	1	0.4882
K	0.240	0.256	0.368	4.2	-0.327	-0.193	0.555	1	0.3947
Rb	0.224	0.226	0.384	4.4	-0.370	-0.195	0.565	1	0.3693
Cs	0.205	0.207	0.366	4.8	-0.420	-0.296	0.770	1	0.3412

was calculated converting the coefficients A_i to the required energy by means of

$$A_i(E) = A_i(\epsilon_F) + B_i(E - \epsilon_F). \quad (\text{A.5})$$

The values of k_F , A_i , and R_M were taken from Ref. 6. The parameters B_i not given in the literature were reconstructed by the Animalu method⁵ using the Abarenkov²¹ and spectral term²² tables. The parameters of the model potential for the Fermi eigenenergies of the elements are given in Table II.

¹Nielsen and Taylor⁴ used a constant pseudopotential, which corresponds to $q = (2/3)k_F$, and linked the thermoelectric power to the experimental values. Our calculations require no adjustable parameters.

²The values given in Ref. 1 do not seem to be sufficiently reliable. This is due to the deficiencies of the measurement method and due to the doubt whether the pure limit was reached or whether the values obtained were affected by residual impurities whose maximum nominal concentrations were as follows: $<10^{-4}\text{Fe}$, $<3 \times 10^{-4}\text{Al}$, $<5 \times 10^{-5}\text{Sb}$, $<5 \times 10^{-5}\text{As}$ (at.%).

³In any case, these do not exceed the Bloch probability w_{e-ph} and, moreover, have no anomalous energy dependence, in contrast to the second-order corrections⁴ in which the distri-

bution function of intermediate electrons occurs in the presence of a phonon in the intermediate state.

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