terpreted as indicating a band-type proton motion in niobium.[10] In this picture of a nondegenerate proton semiconductor the temperature dependence of the diffusion constant is given by that of the proton concentration in the conduction band. The stronger temperature dependence for deuterium can be attributed to a larger bandgap. However, it is also possible that for deuterium, compared with hydrogen, the next higher band gives the main contribution to deuteron conduction. A discussion of the isotope dependence of D_0 in the band model requires a more detailed knowledge of the band properties. A realistic theoretical band model for the proton mobility will have to take into account the local lattice distortion caused by the proton when located in interstitial sites. Therefore, a model similar to the polaron appears to have a good chance for a successful description of the results.

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LOW-TEMPERATURE THERMOPOWER OF DILUTE ALLOYS*

P. E. Nielsen† and P. L. Taylor
Department of Physics, Case Western Reserve University, Cleveland, Ohio

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A new mechanism—the virtual recoil of solute ions—is investigated and shown to cause the dominant contribution to the thermopower of dilute alloys at low temperatures.

The fact that the magnitude and sign of the thermopower of dilute alloys is a strong function of the specific type of solute present has been well established,[1-6] and has long been an unsolved theoretical problem. In this Letter, it is shown that a major contribution to the low-temperature thermopower arises from the virtual recoil of the solute ions. Using a free-electron model we indicate how by taking this mechanism into account qualitative agreement between theory and experiment can be obtained for alloys of alkali metals in K.

The electron-diffusion thermopower S is given to first order in temperature T by the well-known relationship[7]

$$S=(\pi^2k^2T/3e)[\partial\ln\sigma(\epsilon)/\partial\epsilon]_{\epsilon=\zeta}, \tag{1}$$

where $\sigma(\epsilon)$ is the conductivity which the sample would have at $T=0$ if the Fermi energy were ϵ and is given by

$$\sigma(\epsilon)=-(e^2/\Omega)D(\epsilon)v^2(\epsilon)\tau(\epsilon). \tag{2}$$

Here Ω is the volume of the sample, $D(\epsilon)$ the energy density of electron states, and $v(\epsilon)$ their group velocity. The relaxation time $\tau(\epsilon)$ is given by

$$1/\tau(\epsilon_{\vec{k}})=\sum_{\vec{k}'}Q(\vec{k},\vec{k}')(1-\cos\theta_{\vec{k}\vec{k}'}), \tag{3}$$

with $Q(\vec{k},\vec{k}')$, the probability per unit time that an electron is scattered from $\vec{k}$ to $\vec{k}'$, given by

$$Q(\vec{k},\vec{k}')=(2\pi/\hbar)|T_{\vec{k}'\vec{k}}|^2\delta(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'}), \tag{4}$$

$T_{\vec{k}'\vec{k}}$ being the transition amplitude for scattering from k to k′. We determine $T_{\vec{k}'\vec{k}}$ taking as our model a gas of free electrons interacting with a random array of impurities through a potential $V(\vec{r}-\vec{l}-\vec{y}_{\vec{l}})$, $\vec{y}_{\vec{l}}$ being the displacement from equilibrium, due to lattice vibrations, of the impurity whose equilibrium position is $\vec{l}$. If for convenience we take $\vec{l}=0$, then in the notation of second quantization the operator V is given to first order in $\vec{y}$ by

$$V(\vec{r}-\vec{y})=\sum_{\vec{k}\vec{k}'}V_{\vec{k}'\vec{k}}c_{\vec{k}'}^{\dagger}c_{\vec{k}}\left\{1+i(\vec{k}-\vec{k}')\sum_{\vec{q},\vec{S}}\left[\frac{\hbar}{2MN\omega_{\vec{q},\vec{S}}}\right]^{1/2}(a_{-\vec{q},\vec{S}}^{\dagger}+a_{\vec{q},\vec{S}})\vec{S}\right\}, \tag{5}$$

where

$$V_{\vec{k}'\vec{k}}\equiv\Omega^{-1}\int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}V(\vec{r})d\vec{r},$$

$c_{\vec{k}}^{\dagger}, c_{\vec{k}}$ are creation and annihilation operators for electrons of wave number $\vec{k}$, and $a_{\vec{q},\vec{S}}^{\dagger}, a_{\vec{q},\vec{S}}$ are creation and annihilation operators for phonons of frequency $\omega_{\vec{q},\vec{S}}$ and polarization $\vec{S}$ in a lattice containing N atoms of mass M. For convenience, we have assumed the masses of solute and solvent to be equal.

To second order in V the amplitude for elastic scattering is found to be

$$T_{\vec{k}'\vec{k}}=V_{\vec{k}'\vec{k}}+\sum_{\vec{k}''}\frac{V_{\vec{k}'\vec{k}''}V_{\vec{k}''\vec{k}}}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}''}}$$

$$+\sum_{\vec{k}''\vec{q}\vec{S}}V_{\vec{k}'\vec{k}''}V_{\vec{k}''\vec{k}}(\vec{k}'-\vec{k}'')\vec{S}(\vec{k}-\vec{k}'')\cdot\vec{S}\left[\frac{\hbar}{2MN\omega_{\vec{q},\vec{S}}}\right]\left[\frac{\langle n_{\vec{q},\vec{S}}\rangle+\langle n_{\vec{k}''}\rangle}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}''}+\hbar\omega_{\vec{q},\vec{S}}}+\frac{1+\langle n_{\vec{q},\vec{S}}\rangle-\langle n_{\vec{k}''}\rangle}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}''}-\hbar\omega_{\vec{q},\vec{S}}}\right]. \tag{6}$$

This expression includes contributions from the processes shown diagrammatically in Fig. 1. We note in (6) that because the energy denominators are different for the scattering processes in Figs. 1(d) and 1(e), we have some terms proportional to the occupancy $\langle n_{\vec{k}''}\rangle$ of the intermediate state. Their derivative near the Fermi surface is large, and provides a major contribution to the thermopower. On the other hand, the other second-order terms are not strongly energy dependent, and subsequently we neglect them. Using (4), we then find

$$Q(\vec{k},\vec{k}')\propto|V_{\vec{k}'\vec{k}}|^2\delta(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'})-\frac{2}{N}V_{\vec{k}'\vec{k}}\sum_{\vec{k}''\vec{q}\vec{S}}V_{\vec{k}'\vec{k}''}V_{\vec{k}''\vec{k}}(\vec{k}'-\vec{k}'')\vec{S}(\vec{k}-\vec{k}'')\cdot\vec{S}$$

$$\times\frac{\hbar^2}{2M}\frac{\langle n_{\vec{k}''}\rangle}{(\epsilon_{\vec{k}}-\epsilon_{\vec{k}''})^2-(\hbar\omega_{\vec{q},\vec{S}})^2}\delta(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'})-\text{c.c.} \tag{7}$$

From (1) and (3), we see that we may restrict our consideration to $\vec{k},\vec{k}'$ on the Fermi surface. In this approximation, the various matrix elements may be taken as functions of the angle between $\vec{k}$ and $\vec{k}'$ only. We write all matrix elements in the form $V_{\vec{k}\vec{k}'}=V_0 g(\theta_{\vec{k}\vec{k}'})$, where V_0 is the matrix element for $\vec{k}=\vec{k}'$ and $g(\theta)$ expresses the angular dependence. Using (7) and (3) and replacing sums over wave vectors by integrals over energy and solid angle $d\Omega$, we find

$$\frac{1}{\tau(\epsilon)}\propto D(\epsilon)\int d\Omega(1-\cos\theta_{\vec{k}\vec{k}'})$$

$$\times\left\{[g(\theta_{\vec{k}\vec{k}'})]^2-\frac{4V_0}{N}\frac{m}{M}\zeta g(\theta_{\vec{k}\vec{k}'})\int d\Omega'\, g(\theta_{\vec{k}'\vec{k}''})g(\theta_{\vec{k}''\vec{k}})(\hat{k}'-\hat{k}'')\cdot(\hat{k}-\hat{k}'')\sum_{\vec{q}}I(\epsilon,\omega_{\vec{q}})\right\}, \tag{8}$$

where it is assumed that $\vec{k}$, $\vec{k}'$, and $\vec{k}''$ are of magnitude k_F (the Fermi radius), and that the phonon frequencies $\omega_{\vec{q},\vec{S}}$ are independent of the polarization $\vec{S}$. We have defined

$$I(\epsilon,\omega_{\vec{q}})\equiv\int\frac{D(\epsilon')f(\epsilon')d\epsilon'}{(\epsilon-\epsilon')^2-(\hbar\omega_{\vec{q}})^2},$$

where $f(\epsilon')$ is the Fermi function, and m, ζ are the electron mass and Fermi energy, respectively. Expanding $I(\epsilon,\omega_{\vec{q}})$ in a Taylor series about the Fermi energy, we find that to first order,

$$I(\epsilon,\omega_{\vec{q}})=I(\zeta,\omega_{\vec{q}})+(\epsilon-\zeta)D(\zeta)/(\hbar\omega_{\vec{q}})^2.$$

We neglect the first term in the expansion as being independent of energy. Using a Debye approx-

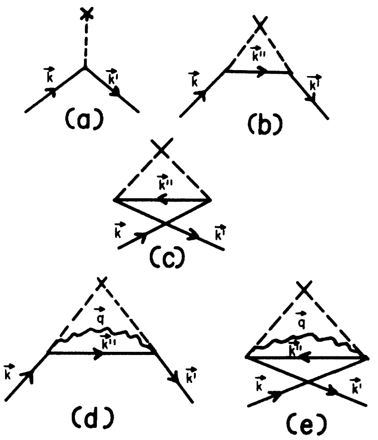

FIG. 1. Elastic scattering processes contributing to the low-temperature thermopower of an alloy.

imation, we perform the sum over phonon frequencies, and find that we may write

$$\frac{1}{\tau(\epsilon)} \propto D(\epsilon)\left[1-\beta\frac{NV_0}{V_1}\left(\frac{\epsilon-\zeta}{\zeta}\right)\right], \tag{9}$$

where $V_1 \equiv (M/m)(\hbar\omega_d)^2/18\zeta$, ω_d is the Debye frequency, and β is a dimensionless constant which arises in performing the angular integrations in (8). Use of (9), (2), and (1) leads directly to the result

$$S = S_0[1+\beta NV_0/V_0], \tag{10}$$

where

$$S_0 = \pi^2 k^2 T/3e\zeta,$$

and is the usual result for the thermopower of free electrons.

We note that while V_0 depends on the solute potential, V_1 depends only on properties of the solvent. For all reasonable values of the parameters involved, $\beta NV_0/V_1$ is of order unity and may be of either positive or negative sign depending on whether V_0 is repulsive or attractive.

As an example, we consider dilute alloys of Na, Rb, and Cs in K. Using the pseudopotentials of Animalu and Heine[8] as quoted by Harrison,[9] we find the parameter ξ $(\equiv S/S_0)$ to take the values shown in Table I. The theoretical results were obtained by renormalizing the pseudopotentials to the atomic volume Ω/N appropriate to the solvent, and taking the difference between the potential of the solute and that of the solvent as the effective potential. The experimental results are those of Guénault and MacDonald[4] for concentrations of 0.2-at.% solute at $T = 3$°K.

Table I. Predicted and observed values for the parameter ξ related to the thermopower of dilute potassium alloys.

Solute	ξ (theory)	ξ (expt)
Na	3.50	0.86
Rb	−0.19	−0.19
Cs	−1.42	−0.43

The mechanism of virtual recoil of the impurities alone is seen to account qualitatively for the experimental results in this system. A more complete calculation would include corrections for a number of other effects, such as the energy dependence of the scattering pseudopotential and the presence of higher order interactions. There are, for instance, processes in which an electron emits a phonon, is scattered by the impurity, and then reabsorbs the phonon; the contribution to S from these processes is independent of the nature of the impurity, however, and is accordingly neglected in this treatment. The effects of these and of multiphonon processes (which are important factors in the high-temperature thermopower) will be included in a more detailed calculation to be published elsewhere.

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