Electrical Resistivity and Thermoelectric Power of Lattice Defects in Metals*

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The electrical resistivity $\Delta\rho$ and the thermoelectric power ΔS of lattice defects in metals consist of a term which depends on the density of the electron states and the electron velocity, and a term which is a function of the electron-scattering cross section of the defects. In metals with an anisotropic Fermi surface, calculations of $\Delta\rho$ and ΔS can be improved considerably if the term depending only on the geometry of the Fermi surface is taken from an experiment which measures its average value over the Fermi surface, rather than from the free-electron model. Calculations of $\Delta\rho$ and ΔS, in which the Fermi-surface term was obtained from the experimentally determined electric size effects, were carried out for vacancies in gold. The term containing the electron-scattering cross section was calculated with the free-electron approximation. The values of $\Delta\rho$ and ΔS obtained in this way are in good agreement with the experimental results. The value of ΔS calculated by using the Fermi-surface term from the free-electron approximation deviates appreciably from the experimental value.

INTRODUCTION

THE electrical resistivity $\Delta\rho$ of lattice defects in metals depends on the electron-scattering cross section of the defects, the density of the electron states, and the electron velocity. The latter two quantities are functions of the geometry of the Fermi surface only. The change ΔS of the thermoelectric power due to lattice defects is a function of the derivative of $\Delta\rho$ with respect to the energy of the conduction electrons. The thermoelectric power of lattice defects is, therefore, given by the variation of the electron-scattering cross section of the defects with the electron energy. It is also dependent on the derivative of the density of the electron states and of the electron velocity with respect to the energy of the conduction electrons. The latter two quantities are again only functions of the geometry of the Fermi surface.

The electrical resistivity[1] and the thermoelectric power[2] of lattice defects in metals has been calculated in the past in a series of papers. The terms containing the electron-scattering cross section of the imperfections have been calculated with the free-electron model in most of these papers. All of the calculations, mentioned above, assumed an isotropic Fermi surface for determining the terms containing the density of the electron states and the electron velocity. However, in metals with an anisotropic Fermi surface the assumption of a spherical Fermi surface may lead to serious errors in the calculation of $\Delta\rho$ and ΔS, even if the free-electron model is valid for calculating the term containing the electron-scattering cross section of the lattice defects. In a rigorous treatment, the electrical resistivity and the thermoelectric power of lattice defects should be calculated by integrating over the Fermi surface. Because of the difficulties of such a calculation, a more simple method using additional empirical information on the terms containing the density of the electron states and the electron velocity is desirable.

The average value over the Fermi surface of the terms in $\Delta\rho$ and ΔS, which contain the density of the electron states and the electron velocity, can be obtained experimentally from the size effect[3] on the electrical resistivity and the thermoelectric power. In the present paper the electrical resistivity and the thermoelectric power of lattice vacancies are calculated. The terms which are only functions of the geometry of the Fermi surface are taken from the experimentally determined electrical size effects. The vacancy is represented by a repulsive square-well potential. The electron-scattering cross section and its dependence on the electron energy are obtained with the free-electron model. The calculations are carried out for gold, for which the most experimental data are available. Gold is, furthermore, particularly interesting since in this metal the Fermi-surface term obtained from the thermoelectric size effect[3] deviates strongly from the free-electron value.

METHOD OF THE CALCULATION

We assume that the metal has a single *isotropic* group of conduction electrons. The electrical resistivity is then given by[4]

$$\rho=\left\{\frac{3}{2e^2n(E)v(E)l(E)}\right\}_{E_F}. \tag{1}$$

Here e is the absolute magnitude of the elementary charge and n the density of the electron states. v, l, and E are the velocity, the mean free path, and the energy of the conduction electrons, respectively. The electrical resistivity of lattice defects is, then, for small defect concentrations

$$\Delta\rho=\left\{\frac{3N_i\sigma(E)}{2e^2n(E)v(E)}\right\}_{E_F}. \tag{2}$$

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] References regarding the numerous calculations on the electrical resistivity of lattice defects may be obtained from K. Fischer, Phys. Status Solidi 3, 2035 (1963) and from J. M. Ziman, Advan. Phys. 13, 89 (1964).

[2] M. F. Abelès, Compt. Rend. 237, 796 (1953); F. J. Blatt, Phys. Rev. 100, 666 (1955); 103, 1905 (1956).

[3] R. P. Huebener, Phys. Rev. 136, A1740 (1964).

[4] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1958).

N_i is the number of defects per volume and σ the momentum-transfer cross section of the imperfections.

For a single isotropic group of conduction electrons the thermoelectric power is[4]

$$S=-\frac{\pi^2 k_B^2 T}{3eE_F}\left\{\frac{\partial \ln l(E)}{\partial \ln E}+\frac{\partial \ln[n(E)v(E)]}{\partial \ln E}\right\}_{E_F}. \quad (3)$$

Here, k_B is Boltzmann's constant, T the absolute temperature, and E_F the Fermi energy. The change in the thermoelectric power due to lattice defects for small defect concentrations ($\Delta\rho \ll \rho$) is then given by[5]

$$\Delta S=S\frac{\Delta\rho}{\rho}\left\{\frac{\partial \ln\Delta\rho/\partial \ln E}{\partial \ln\rho/\partial \ln E}-1\right\}_{E_F}. \quad (4)$$

We are here only concerned with the electron-diffusion component of the thermoelectric power and do not consider at all the phonon-drag component. With Eqs. (1), (2), and (3) we obtain from Eq. (4)

$$\Delta S=\frac{\pi^2 k_B^2 T}{3e}\frac{\Delta\rho}{\rho}E_F \times\left\{\frac{\partial \ln\sigma(E)}{\partial \ln E}-\frac{\partial \ln[n(E)v(E)]}{\partial \ln E}\right\}_{E_F}-S\frac{\Delta\rho}{\rho}. \quad (5)$$

As seen from Eq. (5) the quantity ΔS depends on the derivatives $\{\partial \ln\sigma(E)/\partial \ln E\}_{E_F}$ and $\{\partial \ln[n(E)v(E)]/\partial \ln E\}_{E_F}$. To simplify the further discussion we introduce the notation

$$A\equiv\{\tfrac{2}{3}e^2 n(E)v(E)\}_{E_F} \quad (6)$$

and

$$B\equiv\left\{\frac{\partial \ln[n(E)v(E)]}{\partial \ln E}\right\}_{E_F}. \quad (7)$$

In a metal with an *anisotropic* Fermi surface, Eqs. (1) to (5) are still valid provided the quantities A, $l(E)$, and $\sigma(E)$ and their derivatives with respect to the electron energy are taken as average values over the Fermi surface. As mentioned above, for calculating the electrical resistivity and the thermoelectric power of lattice defects the free-electron values of A and B have been used in the past. However, the average values of A and B, which depend only on the geometry of the Fermi surface, may deviate appreciably from the free-electron values. By using the free-electron values of these quantities, one may introduce appreciable errors in the calculation of $\Delta\rho$ and ΔS. These errors can be eliminated if a more correct value of the quantities A and B is used in the calculation.

The average value over the Fermi surface of A and B can be obtained directly from experiment through the size effect on the electrical resistivity and the thermoelectric power.[3] Using these experimentally determined values, the quantities $\sigma(E_F)$ and $\{\partial \ln\sigma(E)/\partial \ln E\}_{E_F}$ remain to be evaluated for the calculation of $\Delta\rho$ and ΔS. For determining $\sigma(E)$ and its derivative with respect to the electron energy we use the free-electron approximation. We assume further that the scattering potential associated with the lattice defect is spherically symmetric. The momentum-transfer cross section of the lattice defects, as obtained by the partial-wave method, is then given by[6]

$$\sigma=\frac{4\pi}{k^2}\sum_{l=1}^{\infty} l\sin^2(\eta_{l-1}-\eta_l). \quad (8)$$

Here k is the magnitude of the wave vector of the electrons at the Fermi surface. η_l are the phase shifts of the asymptotic solutions of the radial part of the Schrödinger equation caused by the perturbation associated with the lattice defect. Here l is the angular-momentum quantum number.

With Eq. (8) we find the derivative

$$\frac{\partial \ln\sigma}{\partial \ln E}=-1+\frac{\sum_{l=1}^{\infty} l\sin[2(\eta_{l-1}-\eta_l)](\partial\eta_{l-1}/\partial E-\partial\eta_l/\partial E)E}{\sum_{l=1}^{\infty} l\sin^2(\eta_{l-1}-\eta_l)} \quad (9)$$

ELECTRICAL RESISTIVITY AND THERMOELECTRIC POWER OF LATTICE VACANCIES IN GOLD

Since the electrical resistivity[7] and the thermoelectric power[5,8] of lattice vacancies in gold have been measured recently with relatively high accuracy, this system is well suited for checking the results of theoretical calculations. We represent the vacancy by a repulsive square-well potential. The radius a of the square well is taken as the atomic radius of gold. The height V_0 of the repulsive square well is obtained from the Friedel condition[9] by assuming that one elementary charge is associated with the scattering potential of the vacancy. The magnitude of the wave vector of the electrons is determined from the Fermi energy with the free-electron model. The parameter values used in the calculation of the electron-scattering cross section of the vacancy are summarized in Table I. The quantity $k_0 a$ given in Table I is defined by

$$k_0^2 a^2=2mV_0 a^2/\hbar^2, \quad (10)$$

where m is the free-electron mass, and $\hbar$ is Planck's constant divided by 2π.

[5] R. P. Huebener, Phys. Rev. **135**, A1281 (1964).

[6] K. Huang, Proc. Phys. Soc. (London) **60**, 161 (1948), Eq. (48).

[7] R. P. Huebener and C. G. Homan, Phys. Rev. **129**, 1162 (1963).

[8] J. Polák, Czech. J. Phys. **B13**, 616 (1963); **B14**, 176 (1964).

[9] J. Friedel, Phil. Mag. **43**, 153 (1952).

TABLE I. Parameter values used for calculating the electron-scattering cross section of lattice vacancies in gold.

E_F	a	ka	k_0a
5.51 eV	1.593×10^{-8} cm	1.9192	1.7870

The phase shifts η_l were calculated using the formula given by Mott and Massey.[10] For obtaining the derivatives $\partial\eta_l/\partial E$ the value of ka given in Table I was varied by about $\pm0.001\%$ and the corresponding phase shifts $(\eta_l\pm\Delta\eta_l)$ were determined. The derivatives $\partial\eta_l/\partial E$ were approximated by the average value of the ratio $\Delta\eta_l/\Delta E$ obtained for the positive and negative change ΔE. The deviation of this average value of $\Delta\eta_l/\Delta E$ from the values calculated for the positive and negative energy variation was less than 0.01%. The calculations of the phase shifts η_l and of the derivatives $\partial\eta_l/\partial E$ were carried out on a CDC-3600 computer.

The average values over the Fermi surface of the quantities A and B were taken from the experimentally determined size effect on the electrical resistivity and the thermoelectric power in gold.[3] These average values and the corresponding values calculated from the free-electron model of a metal are given in Table II.

The calculated and the experimental values of the electrical resistivity and the thermoelectric power of vacancies in gold are summarized in Table III. The table also includes the calculated values of $\Delta\rho$ and ΔS which are obtained using the quantities A and B from the free-electron model.

DISCUSSION

As seen from Table III, the electrical resistivity and the thermoelectric power of vacancies calculated with the values of A and B from the electric size effects are in good agreement with the experimental results. The value of $\Delta\rho$ obtained with the function A from the free-electron model is also in agreement with the experimental value. However, the thermoelectric power calculated with the function B from the free-electron model deviates appreciably from the experimental result. The error introduced into the calculation by using the free-electron value of B is still more pronounced in the quantity $\partial\ln\Delta\rho/\partial\ln E$, which is wrong by an order of magnitude and also has the wrong sign. This drastic error is, of course, due to the large difference between the values of B obtained from the free-electron model and from the electric size effect (Table II). In the case of vacancies in gold, the first term in Eq. (5) is smaller by an order of magnitude than the second term. Therefore, the thermoelectric power ΔS is relatively insensitive to an error in the quantity $\partial\ln\Delta\rho/\partial\ln E$.

The value of $\partial\ln\Delta\rho/\partial\ln E$ calculated with A and B from the free-electron model and given in Table III is in disagreement with the value of -0.3 calculated by Abelès.[2] Abelès used the same parameter values of ka and k_0a as the present calculation and obtained the functions A and B from the free-electron approximation.

TABLE II. Average values over the Fermi surface of the quantities $A=\{2e^2n(E)v(E)/3\}_{E_F}$ and $B=\{\partial\ln[n(E)v(E)]/\partial\ln E\}_{E_F}$ in gold.

	From the electric size effects[a]	From the free-electron model
A ($10^{11}\,\Omega^{-1}$ cm^{-2})	1.04 ± 0.17	1.20
B	-1.05 ± 0.19	$+1.0$

[a] See Ref. 3.

[10] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1952), p. 38.

TABLE III. Calculated and experimental values of the electrical resistivity, the thermoelectric power, and the derivative $\partial\ln\Delta\rho/\partial\ln E$ for lattice vacancies in gold.

	$\Delta\rho\left(\frac{\mu\Omega\text{cm}}{\text{at\%}}\right)$	$\frac{\Delta S}{\Delta\rho}\left(10^5\frac{\mu\text{V}}{^\circ\text{K}\Omega\text{cm}}\right)$	$\frac{\partial\ln\Delta\rho}{\partial\ln E}$
Calculated with A and B from the electric size effects	1.66 ± 0.27	-7.45 ± 1.16	$+0.36\ \pm0.19$
Calculated with A and B from the free-electron model	1.44	-20.0	-1.69
Experimental value	$1.8\ \pm0.4$[a]	-9.24 ± 0.19[b]	$+0.071\pm0.032$[b]

[a] See Ref. 7.
[b] See Ref. 5.

Therefore, his value of $\partial\ln\Delta\rho/\partial\ln E$ seems to be affected by a numerical error in the calculation.

The present calculation indicates that the use of the free-electron value of the function B leads to an appreciable error in the calculation of the thermoelectric power of lattice vacancies in the noble metals. The calculation of the thermoelectric power of lattice vacancies can be improved considerably if the average value of the function B over the Fermi surface, as obtained experimentally from the thermoelectric size effect, is used. The free-electron approximation seems to work reasonably well for calculating the scattering cross section of vacancies and its dependence on the electron energy. These conclusions can be expected to be generally valid for defects in metals with an anisotropic Fermi surface.

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