High-temperature thermoelectric power and electrical resistivity of single-crystal rhenium and their relation with the electronic structure

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The thermoelectric power and electrical resistivity of a rhenium single crystal have been studied at temperatures between 77 and 1600 K and between 300 and 1600 K respectively. Measurements were made for the two principal crystallographic directions: parallel and perpendicular to the hexagonal axis of the crystal. A sharp change in the temperature dependence of the thermoelectric power close to 400 K and its strong anisotropy at higher temperatures have been found. An explanation of these phenomena is given based on a consideration of the specific properties of the electron energy spectrum and the Fermi surface of rhenium.

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It has been shown that the temperature dependence of the thermopower of many transition metals is very complicated, even at high temperatures.[1,2] This is in marked contrast to the deductions from the theory of nearly free electrons, which is normally considered to be well applicable at high temperatures. There is as yet no explanation of the reasons for the departure of the temperature dependence of thermopower from the predictions of the simple model. It may be important that the real Fermi surface of most metals is appreciably more complicated than the simplest spherical surface considered in the nearly-free-electron approximation. For metals with an anisotropic crystal structure, a comparison of the singularities and anisotropy of thermopower with the singularities and anisotropy in the electron energy spectrum could aid the understanding of the role of the geometry of the Fermi surface in producing complex temperature dependences of the thermopower. However, until recently there have hardly been adequate results on the high-temperature thermopower of single-crystals of anisotropic metals.

Rhenium is an interesting material to study because it has a hexagonal structure with no polymorphic transformations up to the melting point (which is very high). We were the first[2] to study the anisotropy in its thermopower S along the principal crystallographic directions. In the present work measurements have been carried out over a considerably wider temperature range: from 77 to 1600 K. The resistivity ρ was measured simultaneously at the same temperatures. The anisotropy of the resistivity of rhenium had previously only been studied[3] at low temperatures (from 2 to 300 K). Our specimens were cut out of one single-crystal ingot and were parallelepipeds of dimensions $2\times2\times10$ mm. The longitudinal axis of each specimen was oriented parallel or perpendicular to the hexagonal crystal axis [0001]. These specimens are denoted respectively by the symbols "||" and "⊥." The thermal and electrical currents for measuring the thermopower and electrical resistivity were directed along the longitudinal axes of the specimens. The purity and perfection of the single-crystal studied is characterized by the resistance ratio for 293 and 4.2 K, $RRR = 130$. Measurements were made in a vacuum of about 1×10^{-5} Torr in two experimental arrangements: one for the temperature range 77–500 K and the second for the range 350–1600 K. The thermopower was measured by a differential method, the resistivity with direct current. These methods require the maintenance of practically constant temperature when reading each experimental point. The time to establish this is long, increasing considerably the measuring time if done "manually." The time during which the experimental system is kept at difficult high temperature conditions is also increased, resulting in a considerable reduction in the quality of the high-temperature measurements. In this work we used an on-line computer system based on an Electronica T3–16M computer, partly described by us earlier.[4,5] This achieves high speed reading and processing of the results of the measurements, which can thus be carried out in the dynamic regime by changing the temperature continuously. The overall time for measurements is considerably shortened and their quality increased: a large number of points can be taken at high temperatures with small random error.

The results of the measurements are shown in Figs. 1 and 2. The behavior of the thermopower demonstrates clearly the existence of the anomaly mentioned above for transition metals: the form of its temperature dependence changes qualitatively near 400 K, while the resistivity has no direct peculiarity in this region. It can also be seen that rhenium

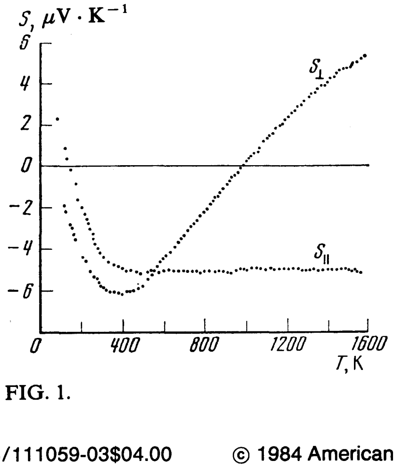

FIG. 1.

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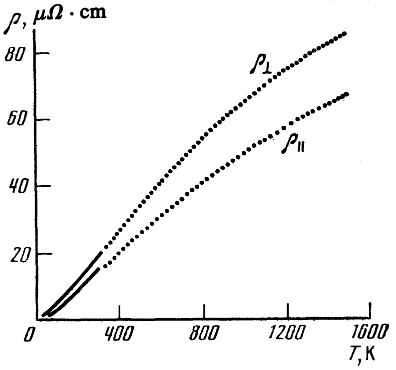

FIG. 2.

was well chosen as a representative of anisotropic metals: the temperature dependences of $S_\perp(T)$ and $S_\parallel$ are very different above 400 K. It is thus necessary to explain the sharp difference in slope of the temperature dependences of $S_\perp$ and $S_\parallel$ of rhenium near 400 K; while for $T<400$ K the difference between $S_\perp$ and $S_\parallel$ is insignificant, it is large for $T>400$ K. It is possible, in principle, to carry out at present a direct numerical calculations of the thermopower of a real metal, starting from data on its electron and phonon spectra. However, for the calculation of such a delicate effect to be reliable, the data on the very complex spectra have to reach an accuracy so far unattainable. It is therefore advisable, as was pointed out at the beginning of this article, to try to establish the qualitative connection between features of the thermopower behavior and features of the electronic structure of rhenium. Data on it can be found in theoretical[6] and experimental[7] works. Analysis of these data made it possible to separate two features important for our purposes. The first is related to the anisotropy of the Fermi surface (FS). According to Mattheis,[6] the FS consists of closed hole sheets in zones 5,6 and 7, open cylinders in zone 8 and electron pockets in zone 9. All these sheets, except for the electron cylinder, are either sufficiently small in size or are characterized by a sufficiently weak anisotropy and cannot, therefore, produce the appreciable anisotropy in electrical properties. For analyzing the thermopower anisotropy, a schematic FS model can therefore be used, in the form of an electron cylinder (Fig. 3). Although this cylinder, in reality, is slightly corrugated, it can be considered as smooth to a first approximation. The axis of the cylinder is directed along the hexagonal axis of the crystal [0001]. We mention the most important property: the distance between cylinders in the repeated zone scheme is roughly equal to the "radius" of the Brillouin zone in a direction perpendicular to [0001]. Second, calculations[6] show and experiment[7] confirms that there is a singularity in the density of states at the Fermi level. It arises as a result of hybridization of s and d states and has an energy width of 0.05–0.10 eV. Its existence shows up in particular in the form of "sleeves" on the cylindrical sheet of the FS, which we have represented schematically in Fig. 3 in the form of small shoulders on the surface of the cylinder.

We shall consider the general expression for thermopower:[8]

$$S=\frac{1}{eT}\frac{K_1}{K_0}. \tag{1}$$

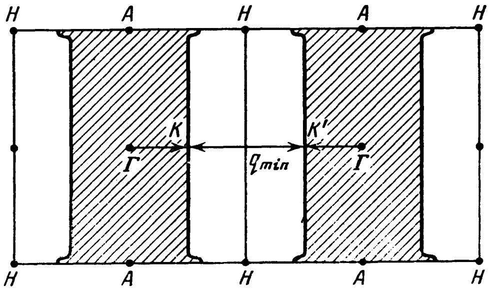

FIG. 3

K_0 and K_1 are here kinetic coefficients which can be written in the form

$$K_0=\int_0^\infty \sigma(\varepsilon)\left(-\frac{\partial f^0}{\partial\varepsilon}\right)d\varepsilon, \tag{2}$$

$$K_1=\int_0^\infty \sigma(\varepsilon)\left(\varepsilon-\varepsilon_F\right)\left(-\frac{\partial f^0}{\partial\varepsilon}\right)d\varepsilon, \tag{3}$$

where $\sigma(\varepsilon)$ is the conductivity of electrons on the equal-energy surface with energy ε. It is useful to consider that the function in Eq. (3) under the integral varies smoothly with energy. In that case, expanding the function in a Taylor series in the neighborhood of the Fermi energy ε_F and limiting it to the first non-vanishing terms, the well known Mott formula for thermopower can be obtained, which is customarily used for calculations:

$$S=-\frac{\pi^2k^2}{3|e|}T\left.\frac{d\ln\sigma}{d\varepsilon}\right|_{\varepsilon=\varepsilon_F}. \tag{4}$$

As can be seen, it does not provide for the possibility of a sharp change in the temperature dependence of thermopower if additional assumptions are not resorted to. The situation is, however, different in the case of rhenium: the existence of a singularity in the density of states near the Fermi level makes the transition from Eq. (1) to Eq. (4) invalid. For a mean width of ~0.07 eV for the singularity, the thermal spread of 2 kT will engulf it at a temperature close of 400 K. On raising the temperature further, the singularity remains entirely within the thermal layer and makes a temperature-independent contribution to the thermopower. The temperature coefficient of the thermopower should therefore decrease (in absolute magnitude) somewhere near 400 K, as is observed in the experimental plots.

To understand why $S_\perp$ and $S_\parallel$ start to depend so differently on temperature above 400 K, it must be remembered that the Debye temperature Θ_D of rhenium is close to 400 K according to different data. Only on approaching this temperature are the shortest-wavelength phonons excited with momentum equal to the limiting momentum, q_D, in the given Brillouin zone. As has been said above, this momentum q_D is about equal to the distance between the FS cylinders in the repeated zone scheme (Fig. 3). The distance between the cylinders determines the minimum wave vector of a phonon, $q_{\min}$, necessary for an electron–phonon umklapp scattering process (U-process) to occur. At temperatures above about 400 K, therefore, umklapp processes start to make a contribution to the scattering of electrons for direction perpendicular to [0001]. They make a contribution to the thermopower with a sign opposite to the sign of the carriers, i.e., it will be a positive contribution for the electron cylinders. Above about 400 K, $S_\perp$ therefore has an appreciable positive slope. The cylinder is open along the [0001] direction, so that there is no defined temperature for *U*-processes to start up and $S_\perp$ is very different from $S_{||}$ above 400 K.

Our results on resistivity tie in well with the low-temperature results.[3] The resistivity anisotropy is relatively small and depends weakly on temperature. There is nothing to object to attributing it to the difference in projected areas of the FS on the planes perpendicular to the corresponding direction.[3] The nature of the factors introduced to explain the anomalies in thermopower explain why the resistivity of rhenium has no corresponding sharp anomalies. The strong influence of these factors on the thermopower is determined by their strong energy dependence near the Fermi level. The resistivity is determined by averages over a range of the order of a few kT of the scattering probability, the density of states, etc., and thus depends weakly on the form of the changes of these quantities with energy.

A specific anlaysis, is of course, necessary to explain anomalies in the thermpower of other metals. However, the results of studying rhenium point to some routes which can also prove successful in other cases. We also note that thermopower is often called the "most sensitive electronic property" of metals.[8] In recent years it has attracted increased attention as a tool for studying the finest details of the electron spectrum and scattering mechanisms. The results of the present work are of interest for this scheme in two directions. First, it provides material for discussing the question of the maintenance of some or other features of the electron spectrum at high temperatures, which have been found or calculated for low temperatures. Second, they may help to find an experimental means of estimating the contribution of umklapp processes to electron scattering.

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