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1992 J. Phys.: Condens. Matter 4 1757

(http://iopscience.iop.org/0953-8984/4/7/013)

J. Phys.: Condens. Matter 4 (1992) 1757–1762. Printed in the UK

The resistivity in high-quality single-crystal palladium

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Received 6 August 1991

Abstract. Measurements of the electrical resistivity in high-purity, single-crystal palladium are presented for the temperature range 17–300 K. A polynomial in temperature is used to describe the data. The results are compared with previous work and the differences are attributed mainly to impurities.

1. Introduction

This paper extends our high-temperature measurements of the resistivity in pure, single-crystal Pd to 17 K [1]. Except for preliminary reports of the present work, previous studies over this temperature range are concerned with material which is not characterized as single-crystal and which is not as pure as is currently available [2, 3]. Smirnov and Timoshenko investigated the resistivity in annealed, 99.98% Pd for the range 77–300 K and reported a kink in the resistivity near 93 K which they attributed to paramagnon ordering [4, 5]. Other work prior to 1979 is summarized by Matula in a CINDAS compilation [6]. More recently, Williams and Weaver reported the resistivity for the 4.2–300 K range in a reasonably pure, annealed rod of Pd with a residual resistance ratio (RRR) of 1340 [7]. In contrast, measurements are presented here for the resistivity of higher-purity Pd in the form of a single-crystral grown from the melt. These values should be close to the intrinsic resistivity because the residual resistivity is so small.

This work was undertaken for several reasons. The resistivity in well-characterized conductors provides information for checking the degree of validity of theoretical models. Indeed, due to the importance of the information it carries about microscopic processes such as the electron–phonon and electron–electron interactions, the resistivity attracts considerable interest, especially in transition metals [8, 9]. Realistic calculations of the resistivity in some of these metals including Pd are now available for comparison with experiment [8, 9]. The very low-temperature measurements of Webb *et al*, however, suggests that electron–electron or electron–paramagnon scattering in this metal may be quite different in the clean and dirty limits [10]. Resistivity measurements for clean, single-crystal Pd over a wider temperature range may therefore lead to a better understanding of the intrinsic transport properties in transition metals.

The present resistivity values are adequately accounted for by electron–phonon scattering at intermediate and higher temperatures. At lower temperatures, other scattering mechanisms generate a significant contribution which seems to be sensitive to defects. There is no evidence for the previously reported kink in the resistivity near 93 K

[4, 5]. This agrees with preliminary studies of the present work and suggests that this anomaly is not intrinsic [2, 3].

2. Experimental methods

The present sample was prepared from 1 mm diameter, 99.999% Pd wire obtained from Johnson, Matthey and Co, London. According to the spectroscopic analysis furnished by the supplier, the metallic impurities present were iron (4 ppm), silicon (2 ppm), calcium (1 ppm), and copper, silver and magnesium, each less than 1 ppm. The wire was etched in aqua regia and washed in distilled water to remove surface contamination. A rod of this material was zone refined in air by the RF floating-zone technique to attain higher purity [11]. The final zone pass formed a nearly uniform, 1 mm diameter, single-crystal rod from which a 4 cm long specimen was cut by spark erosion. Laue back-reflection photographs of this sample showed no appreciable substructure.

The resistivity measurements were carried out using an APD Displex closed-cycle He refrigeration system, model CSA202. A model APD-B temperature controller stabilized the temperature to within 0.1 K. The sample was mounted on an oxygen-free copper sample holder that was attached to the second stage of the refrigerator. The sample holder was enclosed in two copper cylinders with the external and internal cylinders attached to the first and second stages of the refrigerator, respectively, to reduce heat radiation from the surroundings significantly.

The sample was attached to the copper sample holder using GE 7031 varnish as an adhesive and cigarette paper as an insulator. Copper current and voltage leads were attached to the sample by means of indium solder. The previously determined resistivity of $(10.55 \pm 0.07)\,\mu\Omega$ cm for pure, single-crystal Pd at 22 °C was used to determine the effective ratio of length to cross sectional area for the present sample [1].

The temperature of this sample was determined from the resistance of a high-quality, platinum crystal of the same size. The thermoresistance was prepared from 99.999% nominal purity, 1 mm diameter Pt wire obtained from Sigmund Cohn, Inc. It was zone refined, grown into a single crystal and attached to the sample holder in the same manner as the Pd sample. The Pt thermoresistance was calibrated using previous data [12].

In addition to the closed-cycle refrigerator measurements, the resistivities of the Pd crystal and the Pt thermoresistance were determined at 4.2 K by immersing the specimens in liquid helium. The residual resistivity of the Pd sample was found using a quadratic temperature extrapolation to absolute zero [7].

3. Results and discussion

Taking into account the accepted theoretical relations for each of the conventional conduction-electron scattering processes, the resistivity, ρ, at low temperatures is given by:

$$\rho = \rho_0 + AT^2 + BT^5 \qquad (1)$$

with the first term corresponding to imperfection scattering, the second to electron–electron or electron–paramagnon scattering, and the last term to electron–phonon scattering [13]. This relation permits the determination of the residual resistivity, ρ_0. Some of the reported values of A are sample dependent, suggesting that this coefficient

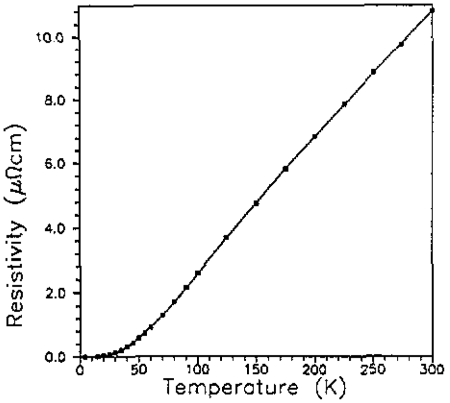

Figure 1. The electrical resistivity in high-quality, single-crystal Pd. The squares represent the present experimental data and the solid line, the least-squares fit given by equation (2).

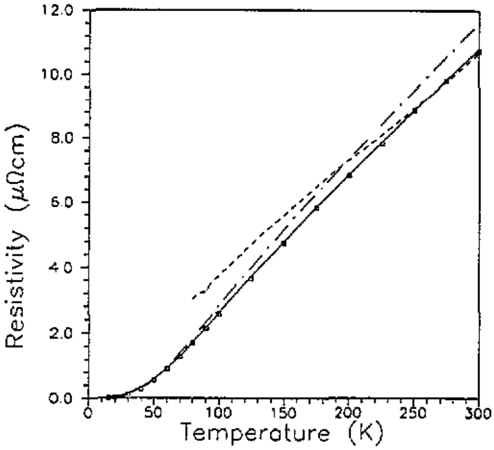

Figure 2. The resistivity in Pd versus temperature—a comparison of theoretical and experimental work. The squares represent the present experimental values; the solid curve, the CINDAS compilation [6]; the dot–dashed curve, the theoretical values of Pinski, Allen and Butler [8]; and the dashed curve, the results of Smirnov and Timoshenko [4, 5], scaled as described in the text.

may be sensitive to impurities and other defects [10]. Assuming the relatively recent values of $A = 2.72 \times 10^{-5}\ \mu\Omega\ \mathrm{cm\ K^{-2}}$ and $B = 6.48 \times 10^{-9}\ \mu\Omega\ \mathrm{cm\ K^{-5}}$ corresponding to the four-probe, DC measurements of Williams and Weaver [7], $\rho_0 = 1.3 \times 10^{-3}\ \mu\Omega$ cm for our specimen. Although it describes the low-temperature resistivity well, equation (1) conflicts with the data at temperatures above 17 K.

An arbitrary fifth-order polynomial can be used to describe the present data at higher temperatures. The corresponding least-squares approximation of the range 17–300 K is given by:

$$\rho = B_0 + B_1 T + B_2 T^2 + B_3 T^3 + B_4 T^4 + B_5 T^5 \tag{2}$$

$B_0 = 0.273\,381\ \mu\Omega\ \mathrm{cm}$ $\qquad B_3 = -5.947\,43 \times 10^{-6}\ \mu\Omega\ \mathrm{cm\ K^{-3}}$

$B_1 = -2.993\,55 \times 10^{-2}\ \mu\Omega\ \mathrm{cm\ K^{-1}}$ $\qquad B_4 = 1.688\,70 \times 10^{-8}\ \mu\Omega\ \mathrm{cm\ K^{-4}}$

$B_2 = 9.748\,00 \times 10^{-4}\ \mu\Omega\ \mathrm{cm\ K^{-2}}$ $\qquad B_5 = -1.832\,20 \times 10^{-11}\ \mu\Omega\ \mathrm{cm\ K^{-5}}$.

Figure 1 shows how well eqution (2) fits the present data. The root mean square error in this approximation of the data is $1.2 \times 10^{-2}\ \mu\Omega$ cm. Equation (2) adequately describes the resistivity between 60 and 300 K without correction. Corrections for equation (2) are given below for temperatures as low as 17 K.

Figure 2 shows the present experimental resistivity values along with those of other investigators [4, 6] and the theoretical results of Pinski, Allen and Butler [8]. This theoretical model (dot–dashed curve) is based on the nearly first-principles determination of a simple formula for the electron–phonon scattering rate using the lowest-order variational solution of the Bloch–Boltzmann equation. The optimal values in this calculation describe the present data reasonably well over most of the range investigated.

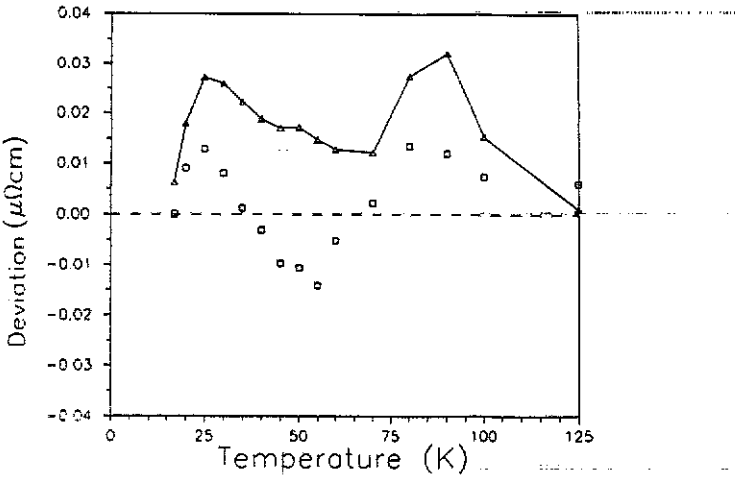

Figure 3. The deviation $\rho_{DATA} - \rho_{EQUATION}$ of the resistivity in Pd from equation (2). The squares represent the present experimental data and the solid line, the CINDAS compilation [6].

The low-temperature T^2 component due to Coulomb scattering or spin-fluctuation scattering seems to be missing above about 60 K because phonon scattering adequately accounts for the magnitude of the resistivity at these temperatures [3]. The theoretical values, however, are about 10% larger than the experimental values near 300 K. It should also be pointed out that up to 700 K this theoretical model is in equally good agreement with our high-temperture measurements [1].

The temperature dependence of the resistivity in Pd, as determined by Smirnov and Timoshenko, deviates a great deal from the present work as shown in figure 2 [4, 5]. Their original values have been scaled by a factor of 9.53 to coincide with ours at 273 K for a comparison of the temperature variation. They have carried out their measurements using a 0.13 mm thick, polycrysalline, plate sample with 99.98% nominal purity. The relatively weak temperature dependence they obtain may be due to the presence of impurities and other defects. The kink in the temperature variation of their values of resistivity near 93 K is absent in the present results, even though an important effort was made to observe such an effect [2].

The solid line in figure 2 represents the CINDAS-recommended values of the resistivity after they were adjusted to correspond to our residual resistivity using Matthiessen's rule [6]. The recommended values apply to annealed 99.99% pure, or purer, Pd and they are based primarily on the data of Laubitz and Matsumura [14], White and Woods [15] and Schriempf [13]. At intermediate and higher temperatures, the present data agree well with the CINDAS-recommended values [6]. The difference is less than 1.5% between 60 and 90 K, and it is less 0.5% in the range 90–300 K. At lower temperatures (<60 K), this difference becomes significant.

The resistivity at these temperatures can be examined more closely using a correction for equation (2). The deviation $\rho_{DATA} - \rho_{EQUATION}$ is shown in figure 3, where ρ_{DATA} represents experimental values and $\rho_{EQUATION}$ is given by equation (2). This deviation is plotted for both the present data and the data recommended by CINDAS adjusted to our residual resistivity using Matthiessen's rule [6]. The deviations are smaller than experimental error above about 90 K, but they are significant at temperatures less than 60 K. The deviations shown in figure 3 should be added to the resistivity given by equation (2) for higher accuracy.

Below about 60 K, our values are significantly smaller than the corresponding CINDAS values as shown in figure 3. The ideal resistivity $\rho_{\mathrm{DATA}} - \rho_0$ for the present data is as much as 22% less than those recommended by CINDAS in the range 17–60 K. The present experimental uncertainty in the resistivity decreases from 5% at 17 K to 3% at 30 K, 1.5 % at 60 K and less than 1% above 90 K. The deviations shown in figure 3 suggest that there may be a rather large positive deviation from Matthiessen's rule in the CINDAS resistivities between 17 and 60 K. The CINDAS compilation uses data for annealed Pd with a RRR in the range 250–600. By contrast, the present work represents a sample of higher purity (RRR > 7000) in the form of a single crystal, grown from the melt and handled carefully to avoid strain. Even though their specimen is not a single crystal, Williams and Weaver report measurements for reasonably pure Pd (RRR = 1340) which are in better agreement with the present measurements than the other previous work [7].

In summary, the resistivity of high-quality, single-crystal Pd is adequately accounted for over a wide temperature range by electron–phonon scattering. At intermediate and higher temperatures the resistivity of well-annealed, polycrytalline Pd of 99.99% purity is very similar to the resistivity in single-crystal material of much higher purity. At lower temperatures, mechanisms other than electron–phonon scattering generate an appreciable contribution to the resistivity. This contribution is sensitive to impurities and possibly other defects. Estimates of the intrinsic resistivity using Matthiessen's rule may not be very accurate below about 60 K for impurity concentrations of the order of 100 ppm or RRRs less than about 600. In higher purity Pd, the low-temperature T^2 component of the resistivity seems to be suppressed rather suddenly in the range 25–60 K. The form of this suppression, however, is not understood quantitatively [2].

Acknowledgments

We are grateful for the numerical values of the theoretical electron–phonon resistivity, which were supplied by Professor F J Pinski. We also appreciate the assistance of Lu Cheng with the numerical analysis. One of us (AK) acknowledges the hospitality of the University of Arizona where the experimental work was carried out.

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