

is on the steep slope of the potential peak on the side of excess silver nitrate. Although the potential change is steeper at more negative potentials, the smaller fluctuations due to slow response to titrant addition led to the choice of this potential. The synchronous motor and the recorder were started and the titrator was set to the "pH-stat" mode. The reaction was followed for 12 h.

Treatment of data. It is easily shown that the consumption V of the titrant is given by

$$V = \frac{v}{n} \int_{t_0}^{t+t_0} x dt \quad (1)$$

where x denotes the concentration of the chemical which is liberated or destroyed during the reaction and which is continuously titrated, v is the flow rate of the reaction mixture and n is the normality of the titrant. For a second-order reaction we have

$$kt = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} \quad (2)$$

where a and b are the initial concentrations of the reactants. This equation gives

$$x = ab \frac{\exp[kt(b-a)] - 1}{b \exp[kt(b-a)] - a} \quad (3)$$

Substitution into eqn. (1) and integration gives

$$V = \frac{v}{n} \left\{ bt - \frac{1}{k} \ln \frac{b \exp[k(t+t_0)(b-a)] - a}{b \exp[kt_0(b-a)] - a} \right\} \quad (4)$$

In the experiment, 72 data points were taken at equal time intervals. Eqn. (4) was fitted to the data by the method of least squares allowing k and t_0 to be adjustable parameters. The sum of least squares was minimized by the general minimization program of Chandler⁴ on a Univac 1108 computer. The standard error of k was estimated using Quenouille's method.⁵ The obtained value, $(5.91 \pm 0.04) \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$, of the rate coefficient at 35°C is in excellent agreement with the value $5.83 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ reported by Peacock and Po Tha.²

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Electrical and Magnetic Properties of PdSb and PtSb

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Many intermetallic phases not only have room temperature electrical resistivities comparable with those of pure metals, but also surprisingly low residual resistivities, implying a high degree of perfection of atomic arrangement in the crystal lattice. The consequently low electron scattering and/or high carrier mobility at low temperatures implies that de Haas-van Alphen oscillations in magnetic susceptibility corresponding to sections of the Fermi surface should be observable; although the interpretation of the experimental data may be difficult in the actual case. The possibility of experimental exploration of the geometry of the Fermi surface in such phases suggests that it could be rewarding to perform electrical and magnetic measurements on suitable representatives.

The present paper concerns the electrical and magnetic properties of PdSb and PtSb, which crystallize¹⁻³ with the NiAs type structure. The PdSb and PtSb phases are reported to exhibit metallic properties,⁴⁻⁶ transformations to superconducting states occurring at 1.5 and 2.1 K, respectively. The de Haas-van Alphen effect has been observed⁷ for PdSb at

liquid helium temperature, but no attempt has been made hitherto to determine its Fermi surface. Judging by the appearances of the relevant parts of the Pd-Sb and Pt-Sb phase diagrams^{3,9} it appeared feasible to obtain suitable single crystals by the zone melting technique.

Experimental. The pure elements used in this study were 99.99 % Pd (L. Light & Co., Ltd.), 99.999 % Pt (Koch-Light Laboratories, Ltd.), and 99.999+ % Sb (Johnson, Matthey & Co., Ltd.). Powder samples were prepared by heating weighed quantities of the components (in the stoichiometric 1:1 ratio) in evacuated and sealed silica tubes. During the syntheses, the temperature was slowly increased to 750°C in the case of PdSb and 1000°C for PtSb, the samples were kept at these temperatures for 7 days, and then quenched in ice water. The sintered powders were finely ground and transferred to new silica capsules which were placed in the zone melting apparatus.⁹ After melting the samples, the temperature was reduced to 770°C in the case of PdSb and 1050°C for PtSb, and the zone heater set in operation so that a zone of ~ 5 mm width was obtained at a speed of 10 cm/h. This technique provided cylindrical single crystal bars of up to 8 mm diameter and 100 mm length. X-Ray and microscopical examination showed that the ingots were essentially single crystals. The PdSb samples consisted of a single phase, whereas a very few small globular inclusions of a second phase occurred in the PtSb samples.

The crystals were cut and ground into rectangular shapes (with approximate dimensions $30 \times 5 \times 3$ mm) for electrical measurements. Single crystal alignment was carried out by standard X-ray methods.

Electrical resistance measurements were carried out according to the four-terminal method, current and potential contacts (copper wire; $\phi = 0.2$ mm) being In-soldered to the specimens. A liquid helium cryostat of conventional design was employed, the sample temperature being controlled automatically and measured by means of a platinum resistance thermometer used in conjunction with an improved Mueller bridge circuit.¹⁰ (A calibrated germanium resistance thermometer was used between 4.2 and ~ 20 K.) The electrical measuring circuit included a Tinsley galvanometer amplifier system as the potential sensing element.

Magnetic susceptibilities were measured between 90 and 1000 K by the Faraday method (maximum field ~ 8000 O) using 40–110 mg samples.

Results. The electrical resistivities of four single crystal specimens of each phase were determined along approximately [001]. (In fact, the specimen axis never deviated from the crystallographic *c* axis by more than 10°. The preferential crystal growth along [001], the dimensions of the zone melted ingots, and the pronounced cleavage properties of the crystals prevented the formation of samples suitable for measurements perpendicular to [001].) The temperature dependence of the electrical resistivity of PdSb and PtSb is shown in Fig. 1. The values are entirely reproducible for conditions of both decreasing and increasing temperature and good agreement is obtained between the results for different specimens of each phase. The residual resistance ratios ($R_{4.2}/(R_{298} - R_{4.2})$) of approximately 1.2×10^{-3} and 7.4×10^{-3} for the measured samples of PdSb and PtSb, respectively, indicate that there is a reasonably high degree of perfection (including purity and stoichiometry) in occupation of lattice sites.

The temperature variation of ρ for PdSb differs from that of PtSb in that the former curve is slightly concave towards the temperature axis (*cf.* Fig. 1). This behaviour appears to be typical for phases comprising palladium and is indicative of *s-d* interband scattering.^{11–13}

The temperature coefficients, $\alpha = (1/\rho_{273})(d\rho/dT)$, calculated from the linear portions of the $\rho(T)$ -curves are $4.0_6 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ (40–150 K) and $3.8_6 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ (180–300 K) for PdSb and $4.0_6 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ (50–300 K) for PtSb.

Using a Grüneisen function, the approximate values of the characteristic temperature θ_R (at a temperature near θ , *cf.* Kelly and MacDonald¹⁴) derived from the $\rho(T)$ -curves are 195 and 265 K for PdSb and PtSb, respectively. The θ_R -values probably differ by no more than a few per cent at the most from the Debye temperature, θ_D , in the region of θ itself.^{14,15}

The magnetic susceptibility measurements show that χ is approximately constant over the temperature interval 90–1000 K for both phases. Field strength dependent susceptibilities were not observed and -0.27×10^{-6} and -0.26×10^{-6} e.m.u./g for PdSb and PtSb, respectively, represent mean values at different field strengths and temperatures. (Excellent reproducibility has been found between various samples of PdSb and PtSb.) The experimental values have not been cor-

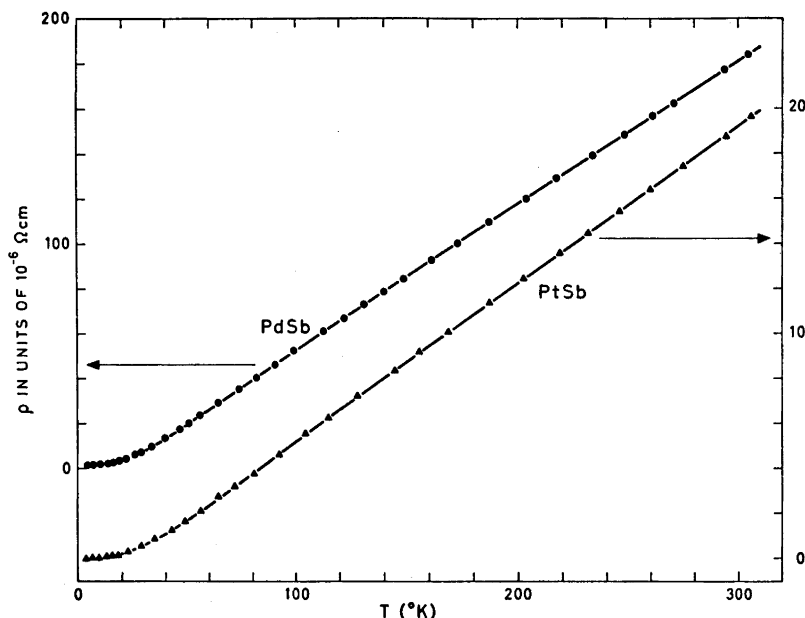


Fig. 1. Electrical resistivity along [001] as a function of temperature for PdSb and PtSb.

rected for induced diamagnetism. Lack of knowledge about the chemical bonding in these phases makes it difficult to give reliable estimates of the correction terms, but according to the empirically deduced^{16,17} core contributions for Pd³⁺, Pt³⁺, and Sb³⁻ the limiting corrections may amount to -0.56×10^{-6} and -0.44×10^{-6} e.m.u./g for PdSb and PtSb, respectively.

The metallic properties of PdSb and PtSb (*vide supra*) clearly exclude the possibilities of filled valence bands at the absolute zero. The number of conduction electrons to be expected is an open question, however. The observed diamagnetism definitely shows that no electrons with unpaired spins are present in the *d* shells of the Pd, Pt, and Sb atoms. Calculations based on a simple model for the magnetic susceptibility suggest, moreover, that there is a small, rather than a large, number of conduction electrons per formula unit in these phases. It is seen, however, that data of this nature appear to afford a rather limited degree of interpretation at the present time.

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