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Abstract. Single crystals of Pd$_2$Si have been grown using a modified cold crucible Czochralski method. The crystals were characterised by x-ray diffraction analysis and density measurements. The resistivity has been measured as a function of temperature (10–1000 K) in the directions parallel ($\parallel$) and perpendicular ($\perp$) to the c axis of the hexagonal structure. Pd$_2$Si behaves like a metallic compound with an anisotropy $\sigma_\parallel/\sigma_\perp = 1.6$ at 293 K (referring to the c-axis direction) and a residual resistivity ratio in the range 130 to 210. The parallel-resistor model has been successfully used to interpret the resistivity data.

1. Introduction

Many results have been published during the last few years on the electrical transport properties of thin film transition metal silicides (Nava *et al* 1987, 1986a, Hensel *et al* 1984, Malhotra *et al* 1984). As regards resistivity, many of these compounds behave like a metal and are characterised by a high value of the residual resistivity ρ_0. This originates from scattering events due to the structural disorder. In the interpretation of the resistivity data, ρ_0 was assumed temperature independent and the Matthiessen additive rule was used, which reads

$$\rho_{ideal}(T) = \rho_0 + \rho_{e-ph}(T) \tag{1}$$

where $\rho_{e-ph}(T)$ represents the electron–phonon scattering contribution to the resistivity. Since in the metallic case, the disorder effect is found, under closer scrutiny, to have a small temperature dependence (Bass 1972), experimental studies on single crystals are desirable for a better understanding of the intrinsic electrical properties of these materials; in fact their residual resistivities are negligible compared with the phonon contribution (Thomas *et al* 1985).

Here Pd$_2$Si has been chosen for its facility to be grown in good crystalline quality and because its electrical transport properties have been already examined on polycrystalline thin films (Wittmer *et al* 1978), so a comparison can be done.

2. Materials preparation and crystal growth

The phase diagram of the Pd–Si system has been studied in detail and a homogeneity range for Pd$_2$Si has been reported by Moffatt (1976).
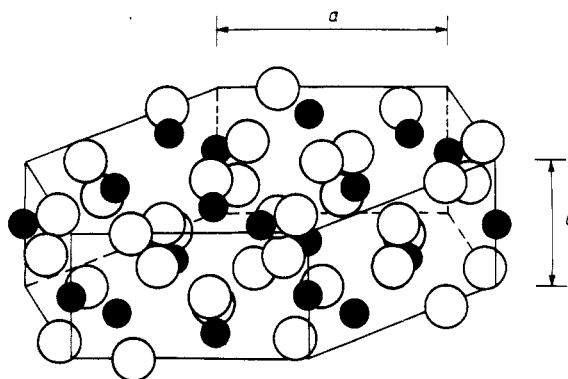
Figure 1. Atomic sites of Si (•) and Pd (○) in the unit cell of the hexagonal Pd_2Si.

Pd_2Si crystallises in an hexagonal structure, represented in figure 1, with parameters $a = 6.496$ Å and $c = 3.433$ Å and melts congruently at 1394°C.

Experimentally, we began preparing bulk samples with Pd/Si atomic ratio equal to 2.00, which corresponds to a composition inside the aforesaid range. This was carried out by melting together suitable amounts of high-purity palladium wires (99.999) and silicon lumps in a conical shaped cold copper crucible, in which the melt was RF levitated, under pure argon at a pressure of 1.5 bar. The crystalline structure and composition of these alloys was checked by x-ray powder diffraction in a Guinier camera using Cu $K\alpha_1$ radiation with silicon as internal calibration standard. The measured lattice parameters are: $a = 6.496$ Å; $c = 3.435$ Å.

Then a polycrystalline bar was obtained in a second crucible by pouring the melted compound in a cylindrical mould. At this point, the Pd_2Si crystals have been grown by the Czochralski technique from a levitated melt using a modified Hukin-type cold crucible. At the bottom of the crucible a cylindrical hole has been opened, in which the polycrystalline bar was set. During the pulling, a cold copper piston pushed the alloy cylinder in the melt at a speed which permitted compensation for the already crystallised volume. The coupling between the liquid mass in the cold crucible and the applied field is strongly dependent on the molten volume (and so is the power supply); our system allows keeping the volume of the liquid constant and pulling from a small liquid zone. Because of lack of a seed, a tungsten needle was used at first for the pulling. By pulling at a rate of about 5 mm h^{-1}, we obtained a large cylindrical single crystal of approximately 7 mm in diameter and 6 cm in length. We measured the lattice parameters again at both ends of the rod, finding the values previously reported; thus we assumed that they were constant through the rod.

The single-crystal rod was then fixed with wax on a goniometric head and oriented by the x-ray Laue diffraction method. After a direction had been determined, slices were cut, by mechanical friction, parallel and perpendicular to the c axis respectively.

The density has been measured for a single crystal by the method of Archimedes, using CCl_4 as the immersion liquid, and we obtained $d_m = 9.50 \pm 0.05$ g cm^{-3}. Using the lattice parameters previously measured and assuming the composition Pd_2Si with three formula units per unit cell, a density $d_c = 9.53$ g cm^{-3} was calculated, in very good agreement with the measured density.

3. Resistivity measurements: results and discussion

Samples were cut from the single-crystal rods. Their typical dimensions were $1 \times 1 \times 6$ mm³. The larger dimension is taken parallel and perpendicular to c axis respectively.

The density of each sample investigated was remeasured, in order to test the presence of voids. The results never differ by more than 1% from the calculated value. Such an effect is thus undetectable and does not affect the absolute value of ρ.

Like other silicides studied (Thomas *et al* 1985, Thomas 1986), Pd₂Si can be easily cut and the final shape of the sample is the desired parallelepipedic one. This leads to a good accuracy in the shape factor and hence in the absolute value of the resistivity which is known with an uncertainty of about 1% in the worst case.

The resistivity was measured *in situ* from 10 to 1000 K by a DC method with the aid of a collinear four point probe consisting of four 0.30 mm diameter tungsten springs spaced approximately 1 mm apart. To avoid erraneous resistivity readings caused by thermovoltages, the measurements were performed for both directions of DC current then averaging the results obtained. The room-temperature resistivities of the samples were also measured *ex situ* with the same small electrodes attached to the corners of the face whose longer edge is in the direction of the resistivity component to be measured. The method described by Montgomery (1971) was used. All resistivity–temperature curves obtained with *in situ* measurements of the resistivity were normalised to the room-temperature resistivity obtained with the aforesaid method. The low-temperature measurements were performed with a variable-temperature cold-end system (Air Products model CS-202). The temperature was measured with a calibrated thermocouple (Scientific Instruments Inc. model C907F Au-0.07 at % Fe/chromel) within ± 0.5 K in the temperature range 10–350 K. For room temperature through to high-temperature measurements, the samples were heated at a rate of 1°C min⁻¹ in a quartz tube furnace with a constant flow of argon purified by passing through a bed of titanium held at 1000°C. The temperature was measured with a calibrated chromel–alumel thermocouple attached to the sample holder and in direct contact with the specimen. The resistivity data were collected by a microcomputer both during the heating and the cooling stages.

Five crystals were examined in this work, each crystal in both directions, and although systematic deviations in ρ versus crystallographic directions were noted, they were extremely small and well within the uncertainty in the geometrical factors ($\simeq 1\%$) of the five crystals.

The results are summarised in table 1 and shown in figure 2. The samples are referred to the corresponding directions, parallel and perpendicular to the c axis, along which the current flows.

Table 1. Summary of the resistivity results for Pd₂Si single crystal ($\rho \perp c$, $\rho \parallel c$).

Samples	ρ(293 K) ($\mu\Omega$ cm)	ρ(10 K) ($\mu\Omega$ cm)	ρ(293 K)$-\rho$(10 K) ($\mu\Omega$ cm)	RRR
$\perp c$	21.00	0.10	20.90	210
$\parallel c$	13.00	0.10	12.90	130

The residual resistivity ratio (RRR), which characterises the amount of defects in the material, ranges from about 130 to 210. This is a fairly high value for a metallic compound and is a test of the good quality of our crystal. The electron–phonon
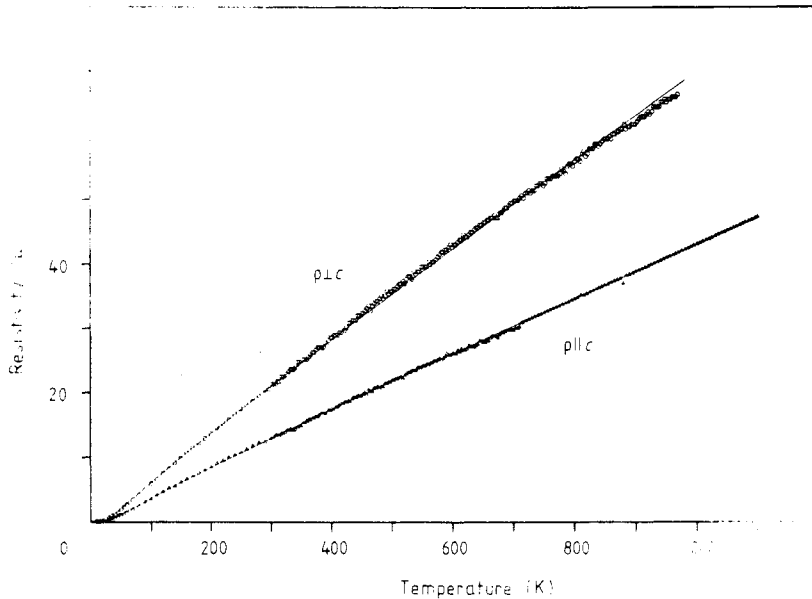
Figure 2. Experimental resistivity data (circles and triangles) and fitting curves (continuous lines) for Pd$_2$Si single-crystal samples oriented perpendicular and parallel to the c axis respectively.

scattering contribution to the total resistivity, $(\rho(293 \text{ K}) - \rho(10 \text{ K}))$, measured when the current flows perpendicularly to the c axis, is almost twice that obtained with the current along the c axis and is very similar to that measured in polycrystalline Pd$_2$Si thin film (Wittmer *et al* 1978).

This equality can be justified by the fact that a structural analysis by TEM on Pd$_2$Si thin films grown on $\langle 111 \rangle$ and $\langle 100 \rangle$ oriented Si substrate revealed that the c axis of the hexagonal structure is perpendicular to the silicon substrate (Wittmer *et al* 1978, Buckley and Moss 1972). Hence studies carried out on the intrinsic electrical transport properties of single crystals, perpendicular to the c axis, and of polycrystalline thin films of Pd$_2$Si, grown on Si substrates, must give similar results.

In both directions Pd$_2$Si behaves like a metal with a sensible difference. In fact whereas with the current along the c axis a linear behaviour is observed in the resistivity curve, perpendicular to the c axis a deviation from linearity (DFL) is present at high temperatures. This DFL, similar to that previously reported for several A15 compounds (Gurvitch 1981, Caton and Viswanathan 1981) and silicides (Nava *et al* 1986b, Mazzega *et al* 1987) has been explained on the basis of the conduction electron mean free path approaching a lower limit with a consequent breakdown of the classical Boltzmann theory (Allen and Chakraborty 1981). To describe this effect the shunt-resistor model has been proposed (Gurvitch 1981):

$$\frac{1}{\rho} = \frac{1}{\rho_{\text{ideal}}(T)} + \frac{1}{\rho_{\text{sat}}} \tag{2}$$

where $\rho_{\text{ideal}}(T)$ is given by (1). ρ_{sat} appears to be independent of temperature and defect concentrations and represents a limiting value in the resistivity saturation phenomenon.

$\rho_{\text{e-ph}}(T)$ in (1) has been approximated with the Bloch–Grüneisen expression

$$\rho_{\text{e-ph}}(T) = \rho' T G(\Theta_{\text{D}}/T)$$

$$G(\Theta_{\text{D}}/T) = 4 \left(\frac{T}{\Theta_{\text{D}}} \right)^4 \int_0^{\Theta_{\text{D}}/T} \frac{z^5}{(\text{e}^z - 1)(1 - \text{e}^{-z})} \, \text{d}z \qquad (3)$$

where ρ' is the high-temperature limit of $\rho_{\text{e-ph}}(T)/T$ and Θ_{D} the Debye temperature.

It must be stressed that the use of the above parallel-resistor formula implies that the low-temperature limit of the measured resistivity is lower than ρ_0. Because this difference is very small, we will not distinguish between the ideal ρ_0 and the measured low-temperature limit of $\rho(T)$ in our analysis.

The experimental data were fitted by a program called FUMILI developed at CERN by Silin (1971). With this program, it is possible to fit the experimental data to any function that can be written in closed form, using an arbitrary number of parameters which are allowed to float. This is done by minimising the square of the deviation of the measured values from the fitting function. The best fitting function was calculated for both the resistivity curves letting the four parameters $\rho_0, \rho', \Theta_{\text{D}}$ and ρ_{sat} in (1), (2) and (3) to float and the values of the best fit parameters are reported in table 2. For illustration, we show in figure 2 the agreement between the experimental data and the calculated curves.

Table 2. Parameters used in equations (1), (2) and (3) to fit the electrical resistivity curves of Pd₂Si single crystal ($\rho \perp c, \rho \parallel c$).

samples	ρ_0 ($\mu\Omega$ cm)	ρ' ($\mu\Omega$ cm K^{-1})	Θ_{D} (K)	ρ_{sat} ($\mu\Omega$ cm)	RMS error ($\mu\Omega$ cm)
$\perp c$	0.01	0.0724	167.64	1604.08	0.0171
$\parallel c$	0.09	0.0445	200.18	935.85	0.0134

It should be mentioned that the success of (2) suggests that it should be a general occurrence, valid in all metals. This does not contradict the data. In cases not showing DFL, like here when the current flows along the c axis, ρ_{ideal} is sufficiently small compared to ρ_{sat} that it is difficult or impossible to detect the extra-conduction channel parallel to the classical Boltzmann channel.

The more striking feature of this analysis is the anisotropy observed in Θ_{D} and ρ.

The fact that the Debye temperature is not a fixed parameter for Pd₂Si, but must be permitted to vary with the crystallographic directions to obtain a close fit to the resistivity data, implies that Pd₂Si cannot be assumed elastically isotropic. Anisotropy of the elastic constants results, in fact, in a dependence of the cut-off frequency on the direction of propagation of the vibrational wave (Blatt 1968).

Similar results have been obtained by best fitting the resistivity data measured along different crystallographic directions of MoSi₂, TaSi₂ and WSi₂ single crystals (Nava *et al* 1989). Moreover, the thermal expansion as a function of temperature along two crystallographic directions '*a*' and '*c*' of MoSi₂ (Thomas *et al* 1985) has been well interpreted with two different values of the Debye temperature, and anisotropic thermal displacements in zinc (Potzel *et al* 1984) have been calculated with two separated Debye models to fit the measured data along the directions parallel and perpendicular to the HCP c axis.

The anisotropy of ρ is remarkable, about 60% at room tempperature. The simplest way to account for this is to assume that the effective area of the Fermi surface contributing to the conductivity is different in the two crystallographic directions.

In such a case, since

$$\rho_{\parallel} = m/e^2 n_{\parallel} \tau_{\parallel}$$

where $n_{\parallel}$ is the number of electrons available for electrical conduction in the direction parallel to the c axis, we can write

$$\rho_{\parallel} \simeq 1/A_{\parallel}\tau_{\parallel}$$

where $A_{\parallel}$ is the only area of the Fermi surface contributing to $\rho_{\parallel}$ and $\tau_{\parallel}$ is the relaxation time appropriate in the resistivity processes present. Using a similar argument we find that $\rho_{\perp} \simeq 1/A_{\perp}\tau_{\perp}$, so

$$a = \frac{\rho_{\perp}}{\rho_{\parallel}} = \frac{A_{\parallel}}{A_{\perp}}\frac{\tau_{\parallel}}{\tau_{\perp}}$$

assuming an equal carrier densities in the two different directions. Hence, if the anisotropy of τ is thought to be less important, it follows the above crude interpretation of the anisotropy in ρ.

However, we recognise that the aforesaid considerations are only speculative and that Fermi surface evaluations along and perpendicular to the c axis should be then desirable in order to estimate the order of magnitude of the anisotropy in the conductivity. Here, we can only outline the fact that the anisotropy parameter, a, equal to 1.6 at room temperature, is of the same order of magnitude of that found for $MoSi_2$ (van Ruitenbeek et al 1987), for tin (Case and Gueths 1970) and for Cd and Zn (Alderson and Hurd 1975) monocrystals.

4. Conclusions

In summary it has been shown that good quality large crystals of Pd_2Si can be grown from the melt. High precision resistivity measurements have been made on these crystals as a function of temperature along the two main crystallographic directions ($\parallel$ and $\perp$ to the c axis). The wide temperature range (10–1000 K) allowed us to observe an anomalous metallic behaviour of ρ when measured perpendicular to the c axis. Its intrinsic resistivity exhibits a negative curvature at high temperatures. This phenomenon has been interpreted by a parallel-resistor model which includes the electron–phonon scattering model of Bloch–Grüneisen to account for the ideal contribution to the total resistivity. The model, of general validity, has been used to interpret the resistivity data for both crystallographic directions, and the best fit to the relative curves is quite good over the entire temperature range. The most striking feature of this study is the anisotropy observed in ρ and Θ_D. The anisotropy of the resistivity has been ascribed to the anisotropy of the Fermi surface areas available for conduction in the directions parallel and perpendicular to the c axis. Resistivity measurements at lower temperatures (≤ 10 K) are in progress in order to examine the temperature dependence of the anisotropy parameter a in the light of the Case–Gueths simplified model of conductivity for anisotropic metals. The anisotropy of

Θ_D has been attributed to an anisotropy of the elastic constants of the compound. Thermal expansion measurements of the crystallographic parameters as a function of temperature are in progress to confirm this hypothesis.

Acknowledgments

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