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The electrical resistivities of liquid Pd–Bi alloys and the band structure of crystalline β -PdBi₂ and PdBi

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Abstract. Measurements of the electrical resistivity ρ of liquid Pd–Bi alloys as a function of temperature have been performed in the concentration range from pure bismuth to 60 at.% Pd. Plotted as a function of composition, the resistivity of Pd–Bi exhibits a maximum near 30 at.% Pd. At this maximum the resistivity reaches a value of 187.6 $\mu\Omega$ cm while the temperature dependence of the resistivity $d\rho/dT$ has a sharp minimum and is almost zero at the same composition. For comparison, calculations of the electronic structure of the crystalline compounds PdBi₂ and PdBi have been carried out using the augmented spherical wave (ASW) method.

1. Introduction

Palladium has a high melting point (1552 °C) and therefore its liquid phase is not easily accessible for physical measurements. Remarkably some of its alloy systems have relatively low melting points up to palladium concentrations of more than 50 at.%. As we formerly have achieved some experience in handling liquid Bi and some of its alloys [1, 2] we decided to select the Pd–Bi system for performing measurements of the electrical resistivity. Figure 1 shows the phase diagram for the bismuth-rich side of the Bi–Pd system [3].

Previously two liquid alloys of the same system (10 and 20 at.% Pd) have been investigated by means of photo-electron spectroscopy measurements [4]. The density of states of pure liquid bismuth shows a strong s–p splitting in addition to a smaller splitting in the p band. When Pd is added Pd d states penetrate the Bi p bands and finally dominate that part of the spectrum.

2. Experimental details

Bismuth ingots, nominal purity 99.999 wt%, were purchased from Ventron GmbH Karlsruhe. Palladium with a nominal purity of 99.9 wt% was obtained from Drijfhout. The sample preparation and the resistivity measurements were carried out in a glove box with oxygen content lower than 1 ppm. For the resistivity measurements, we used the metal tube method described previously in a paper dealing with liquid alkali–Bi

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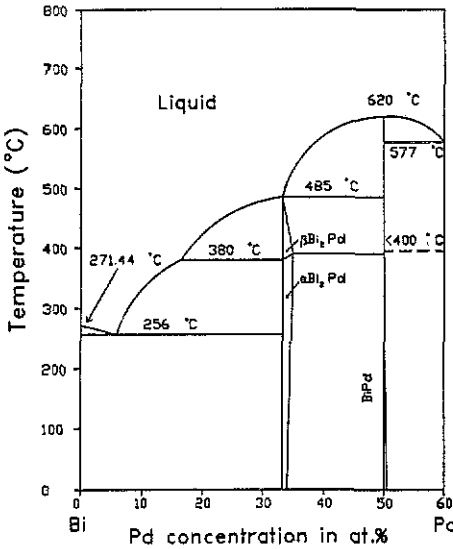


Figure 1. Part of the phase diagram of the Pd-Bi system. Reproduced, with permission, from [3].

alloys [2]. It is our experience [5] that this method gives excellent results provided the resistivities are low (typically $< 1000 \mu\Omega \text{ cm}$) and corrosion and evaporation problems are absent. An alternative but, according to our experience, usually slightly less accurate method makes use of an insulating cell (e.g. alumina) provided with electrodes. In the case of some Pd-Bi alloys, for unknown reasons, alumina turned out to be mechanically unstable.

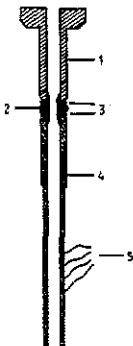


Figure 2. The measuring tube. 1: AISI 321 stainless steel tube; 2: tantalum junction; 3: Pd₆₀Ni₄₀ (wt%) solder; 4: molybdenum tube; 5: molybdenum electrodes.

At the temperatures at which the measurements were performed the solubility of the AISI 321 stainless steel tubes in the Pd-rich alloys proved to be too high. Corrosion tests showed that molybdenum tubes are perfectly suitable. This implied that the molybdenum tube had to be connected to the stainless steel tube leading to the pumping system. Because the thermal expansion coefficients of molybdenum and stainless steel differ considerably, a direct weld could cause leaking problems at high temperature. Therefore tantalum was used as a junction material. A high-

temperature solder, a mixture of 60 wt% Pd and 40 wt% Ni was applied. A good connection could be obtained by brazing with a high-frequency generator. The tube proved to be vacuum-tight at the temperatures required for the experiment. The molybdenum tubes originally had an inner diameter of 3 mm and an outer diameter of 4 mm. In order to increase the accuracy of the measurements, the wall thickness of the tube was reduced to 0.25 mm by lathing. As electrodes four molybdenum wires were point-welded to the measuring tube. A schematic diagram of the measuring tube is shown in figure 2. The final values of the resistivities are the averages of the measurements on three tube sections each of approximately 2 cm length. The agreement between the results from the three tube sections was typically within 0.2%, with exceptionally high values (0.5, 1.0 and 0.5%) for the samples with 5, 10 and 15 at.% Pd respectively. The time stability of the measurements was excellent. We could use a thin-walled stainless steel tube for the alloys with less than 20 at.% Pd as no significant corrosion by Bi-rich alloys occurred. The results obtained from the two kinds of tube were in good mutual agreement. Owing to the high melting temperature of Pd, the measurements had to be restricted to alloys with less than 60 at.% Pd. All the resistivity data for this system were obtained from empty tube measurements, calibration measurements and measurements on the tube filled with the sample. Pb with a small amount of Na was used as a reference material for calibration. All procedures were checked by measuring pure liquid Bi before starting the investigation of the liquid Pd-Bi alloys. The new resistivity data for pure bismuth reproduced the former ones within 0.2% [2].

3. Results

The experimental electrical resistivities of liquid $\text{Pd}_x\text{Bi}_{1-x}$ alloys as a function of temperature are shown in figure 3(a) for $x \leq 0.30$ and figure 3(b) for $x \geq 0.33$, respectively. Figure 4 gives interpolated results as a function of composition for different temperatures. In figure 5 values of $d\rho/dT$ are given in the same way. Most of our results were fitted to second-degree polynomials in T . The relative error in the resistivities is $\pm 0.3\%$, the absolute error in the $d\rho/dT$ typically $\pm 0.002 \mu\Omega \text{ cm K}^{-1}$, with a few exceptionally high values for Pd concentrations of 38 and 40 at.% (± 0.005 and $\pm 0.006 \mu\Omega \text{ cm K}^{-1}$, respectively). It should be noted that $d\rho/dT$ is small (of the same order as in simple liquid s-p metals) and that, therefore, it is not an easily measurable quantity. From figure 4 it is seen that the resistivity of the Pd-Bi system exhibits a pronounced maximum, with a value of $187.6 \mu\Omega \text{ cm}$ at 700°C . The composition corresponding to this maximum is approximately 30 at.% Pd. The temperature derivative $d\rho/dT$ has a distinct minimum and is almost zero at this composition. For higher Pd concentrations $d\rho/dT$ first has a sharp maximum and then falls steeply to negative values.

4. Band structure calculations and discussion

The band structure of crystalline $\beta\text{-PdBi}_2$ was calculated using the augmented spherical wave (ASW) method by Williams *et al* [6]. Scalar-relativistic effects were included as described by Methfessel and Kuebler [7]. Spin-orbit interaction was incorporated by adding the $L \cdot S$ operator to the final Hamiltonian, using spin-orbit parameters

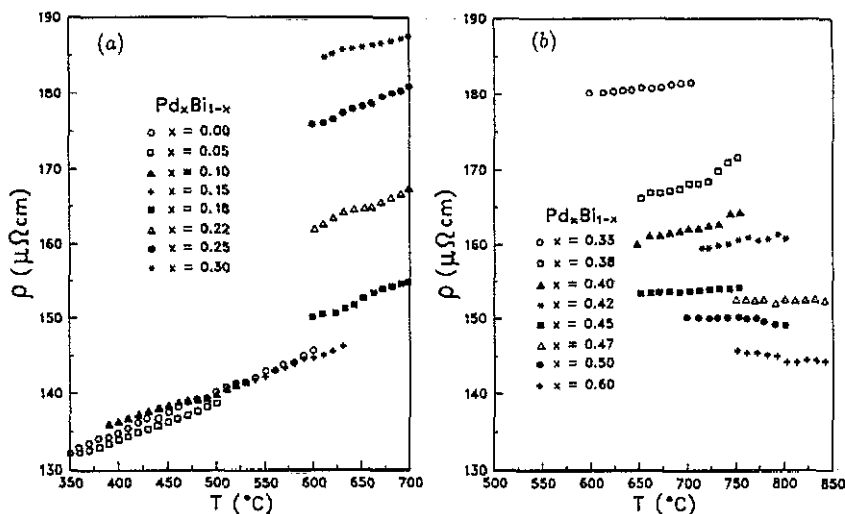


Figure 3. Experimental electrical resistivities of liquid $\text{Pd}_x\text{Bi}_{1-x}$ alloys as a function of temperature: (a) $x \leq 0.30$; (b) $x \geq 0.33$.

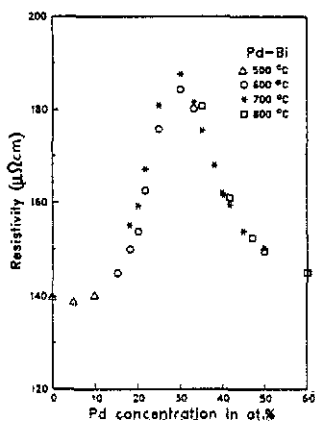


Figure 4. The resistivity ρ of liquid Pd-Bi alloys as a function of composition at the temperatures indicated in the figure.

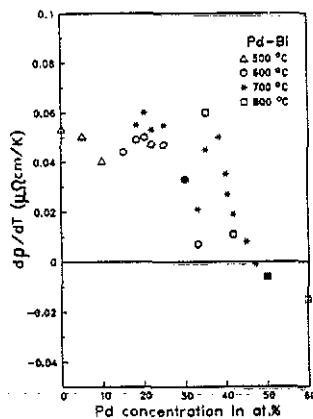
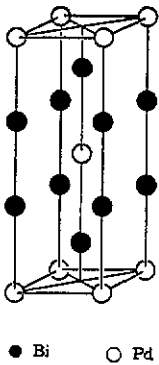


Figure 5. The temperature dependence of the resistivity $d\rho/dT$ of liquid Pd-Bi alloys as a function of composition at the temperatures indicated in the figure.

from atomic spectroscopy. The basis set employed 4d, 5s and 5p functions for Pd and 6s, 6p and 6d functions for Bi with the inclusion of 4f functions for Pd and 5f functions for Bi in the three-centre terms (which can be regarded as treating these states in a perturbative way). The calculation was performed for the high-temperature form of PdBi_2 , also referred to as the β -phase (Space group, $I4/mmm$, No 139 in the *International Tables for Crystallography*; Pd in 2a and Bi in 4e with $z = 0.363$). The primitive unit cell contains one formula unit. The crystal structure [8] consists of square layers of Pd and Bi stacked in the z direction with sequence Pd-Bi-Bi etc

Figure 6. The crystal structure of β -PdBi₂.

(see figure 6).

The band structure is shown in figure 7 while figure 8 shows the density of states as a function of energy. There are two bands of exclusively Bi s character off the panel of figure 7 which have been omitted for visual clarity but which are shown in figure 8. The positions are in good agreement with the photoemission results. From 5 eV below E_F up to E_F there is a complex of primarily Pd d and Bi p character. The Pd partial density of states shows peaks at -2.9 eV and -3.7 eV. The Bi partial density of states shows less pronounced structure. These features are well resolved by the photoemission results [4].

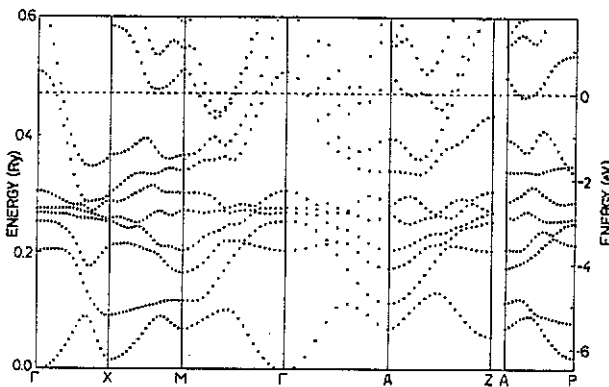


Figure 7. The band structure of β -PdBi₂. The broken line corresponds to the Fermi energy.

A very distinct feature is the pseudo-gap in the density of states curve just 0.6 eV below E_F . Its origin is explained by the band-structure plot: at these energies the intersections of bands 11 and 12 vanish and the only intersections left are the ones of band 9 and 10 and then only for a few directions in the Brillouin zone.

The crystal structure of PdBi shows similarities as well as essential differences as compared with that of PdBi₂. The structure [8] is characterized by planes of Bi atoms, similar to those in PdBi₂ but with distortions. The double layers of Bi are alternated by double layers of Pd as compared with the single Pd layers in PdBi₂.

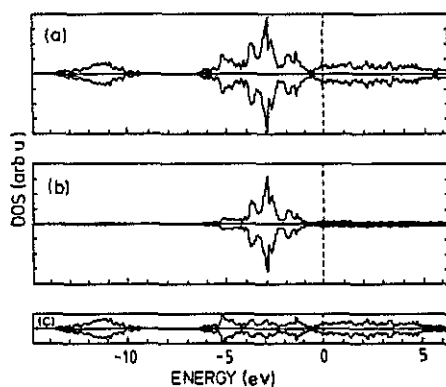


Figure 8. The density of states of β -PdBi₂: (a) the total DOS; (b) the partial DOS of Pd; and (c) the partial DOS of Bi.

As a result, the stacking of the layers is altered. One consequence of this is the seven-coordination of Pd by Bi and *vice versa*. A crucial difference is the occurrence of short Pd–Pd distances in PdBi between palladium atoms in neighbouring planes (2.70 Å), even shorter than the Pd–Pd distance in elemental palladium (2.75 Å). The Pd–Pd distance in PdBi₂ is 3.362 Å in the planes and is 6.9 Å along the z direction. The resulting strong Pd–Pd interaction in PdBi is directly reflected in the results of the calculated electronic structure for this compound. The Pd d electrons in PdBi contribute to the density of states at the Fermi energy, unlike in PdBi₂. As a consequence the density of states at E_F is greatly enhanced in PdBi (16 states (Ryd.formula unit)⁻¹) and no pseudo-gap like that in PdBi₂ exists. We have not included a band-structure diagram nor a density of states plot for PdBi, as the latter is not particularly informative.

Returning to the electrical resistivity results we make the assumption that the electronic structure just above the melting point is still closely related to the electronic structure of the corresponding solid phases (in the case of PdBi₂ this is the high-temperature phase). It is then plausible to assume that the conductivity minimum at the Bi-rich side of the composition PdBi₂ in the liquid phase is connected with the position of the Fermi energy in the minimum in the density of states found for PdBi₂ (figure 8).

The minimum in $d\rho/dT$ accompanying the maximum in ρ is a frequently observed phenomenon. Mooij [9] noted that small and even negative values of $d\rho/dT$ occur in alloys containing transition metals if ρ exceeds values of 100–150 $\mu\Omega$ cm. In many ionic alloys (see, e.g. references in [10]) $d\rho/dT$ changes sign for values of ρ of the order of several hundreds of $\mu\Omega$ cm. The precise mechanism in the liquid Pd–Bi alloys is not known as yet.

The behaviour of $d\rho/dT$ for concentrations larger than 40 at.% Pd is quite unusual. There is a sharp maximum and then again a steep fall to negative values. From the band-structure calculations on BiPd it follows that the minimum in the density of states found for PdBi₂ and assumed to be responsible for the conductivity minimum disappears for higher Pd concentrations. This explains the fall of the resistivity in that composition range, but unfortunately not the negative $d\rho/dT$ found for 50 and 60 at.%. It should once more be noticed that the behaviour of $d\rho/dT$ is indeed significant from an experimental point of view, but that the actual values

of $d\rho/dT$ are small and consequently the effects rather subtle. Also, $d\rho/dT$ is a far more delicate quantity to explain theoretically than ρ itself and more background information may be needed to explain the change of sign.

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