Journal of Alloys and Compounds, *176* (1991) 1–6
LCM 1284

High pressure phase $PtPb_2$: synthesis, structure and properties

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(Received January 18, 1991)

Abstract

The new phase $PtPb_2$ was prepared at high pressure (7.7 GPa) and temperature (1300–1500 K). Determination of the structure showed that it had the $CuAl_2$-type structure (space group $I4/mcm$, $Z=4$) with tetragonal unit cell parameters $a=6.934\pm0.003$ Å, $c=5.764\pm0.003$ Å. The heat of decomposition H and the activation energy of this process E were measured at normal pressure: $H=8.7\pm0.6$ kJ mol^{-1}, $E=108\pm7$ kJ mol^{-1}. The new phase transformed into the superconducting state at $T=3\pm0.2$ K. The band structure, density of states and volume, the dependence of the total energy of the new phase were calculated using the LMTO method.

1. Introduction

It is known from the Pt–Pb equilibrium diagram [1] that the phase of $PtPb_2$ with $CuAl_2$-type structure (C16) does not exist at normal pressure. It has been shown in a substantial review [2–5] of the synthesis, the analysis of instability and the properties of intermetallic phases with $CuAl_2$-type structure that there is a possibility that a $PtPb_2$ phase with this structure exists. Unsuccessful attempts to prepare this phase at normal pressure were also reported.

This compound may be synthesized by high pressure and high temperature methods because a rather large (about 10%) contraction accompanies the formation process of the known $CuAl_2$-type compounds (for example $RhPb_2$ and $PdPb_2$).

2. Experimental procedure

The experiments were performed in a high pressure "toroid"-type chamber [6]. Phase transitions in bismuth at 2.55, 2.69 and 7.7 GPa were used to calibrate the chamber. The alloys were prepared from mixtures of lead and platinum (purity 99.9%). The starting composition corresponded to the formula $PtPb_2$ (66.7 at.% Pb). A well mixed powder of the metals was compressed

0925-8388/91/$3.50

and placed in a glass graphite heater. The temperature was controlled by a chromel–alumel thermocouple located externally near the heater wall. The mixtures were heated at constant pressure and temperature for periods of 30 min and then quenched. After the high pressure and high temperature treatment the samples were examined under normal conditions.

The phases present were determined by X-ray diffraction using a Geigerflex diffractometer with Cu Kα radiation. The composition of the alloys was determined by X-ray microanalysis (MAR-1) with an accuracy of ±3 at.%.

Quantitative thermal analysis was performed using a commercial derivatograph "C" (MOM, Hungary) and isochronal annealing with different heating rates.

The electrical resistance of the samples was measured at low temperatures to determine the superconducting transition temperature.

3. Experimental results

The experiments were carried out at 3.5 and 7.7 GPa at different temperatures up to 1500 K. The new phase $PtPb_2$ was only obtained at $p = 7.7$ GPa in the temperature range 1300–1500 K. The X-ray powder data were indexed on the basis of a body-centred tetragonal unit cell with parameters $a = 6.934 \pm 0.003$ Å, $c = 5.764 \pm 0.003$ Å (see Table 1). These data led us to assume that the phase $PtPb_2$ has the $CuAl_2$-type (C-16) structure (space group $I4/mcm$, $Z = 4$). The density calculated from the X-ray data was 14.6 g cm^{-3} which is in good agreement with the pyknometric density 14.4 ± 0.2 g cm^{-3}.

The initial value of the atomic parameter X_{Pb} was determined using the Paterson one-dimensional function. Subsequently, the minimum value $R = 0.20$ was found by the least squares method for $X = 0.165$. The nearest neighbour coordination numbers and the interatomic distances are listed in Table 2.

Isochronal annealing with heating rates 7, 12 and 20 K min^{-1} was used to investigate the behaviour of the new phase $PtPb_2$ at normal pressure and high temperatures. It was found that there is an isothermal peak in the temperature range 370–444 K resulting from the decomposition of $PtPb_2$ into the well known phases PtPb and $PtPb_4$. The heat of decomposition was $H = 8.7 \pm 0.6$ kJ mol^{-1}.

The value of the activation energy for the decomposition process was calculated from the expression:

$$E = R\frac{T_1 T_2}{T_1 - T_2} \ln \frac{T_2^2 V_1}{T_1^2 V_2}$$

where R is the gas constant and T_1 and T_2 are the decomposition temperatures at the heating rates V_1 and V_2 respectively. The value of the activation energy was found to be $E = 108 \pm 7$ kJ mol^{-1}.

The new phase $PtPb_2$ was found to be a superconductor with $T_c = 3.0 \pm 0.2$ K. The other compounds with $CuAl_2$-type structure formed from lead and

TABLE 1

X-ray data of the new phase $PtPb_2$ ($CuAl_2$-type)

N	*hkl*	I/I_0	*d*(measured) (Å)	*d*(calculated) (Å)	*F*(measured)	*F*(calculated)
1	110	3	4.89	4.902	16.4	14.4
2	002	8	2.880	2.882	40.0	36.0
3	211	79	2.731	2.730	47.2	52.1
4	112	20	2.482	2.484	37.3	51.1
5	220	20	2.450	2.451	53.6	44.0
6	202	100	2.217	2.216	95.2	68.4
7	310	13	2.190	2.192	34.7	76.1
8	222	3	1.868	1.867	20.2	21.3
9	312	3	1.740	1.745	15.5	3.6
10	400	3	1.731	1.733	31.3	10.9
11	330	21	1.634	1.634	71.0	86.1
12	213			1.633		
13	411	23	1.615	1.614	66.9	44.1
14	420	14	1.553	1.550	54.9	50.2
15	402	15	1.482	1.485	84.7	83.1
16	004	5	1.440	1.441	71.4	95.1
17	332	17	1.422	1.422	67.2	93.3
18	422	3	1.367	1.365	17.1	13.0
19	510	3	1.358	1.359	32.9	28.0
20	323			1.359		
21	413	5	1.266	1.265	29.4	39.1
22	521	18	1.256	1.256	56.3	51.6
23	512	16	1.229	1.230	97.3	91.5
24	440			1.226		
25	314	11	1.204	1.204	45.9	59.6
26	530	10	1.1888	1.1891	62.6	46.4

TABLE 2

Interatomic distances

	Atom	Number of neighbours	Interatomic distance
[$PtPt_2Pb_8$]	Pb	8	2.99
	Pt	2	2.88
[$PbPt_4Pb_{11}$]	Pt	4	2.99
	Pb	1	3.24
	Pb	2	3.33
	Pb	4	3.68
	Pb	4	3.66

transition metals have similar critical temperatures: $T_c = 3.0$ K($PdPb_2$), $T_c = 3.1$ K ($AuPb_2$) [6].

4. The band structure and density of states calculations

The aim of this part of the work was to analyse the theoretical stability of the (tetragonal) new phase $PtPb_2$. The calculations were performed using the self-consistent LMTO method for frozen cores with local density functional approximation using the Barth–Hedin exchange-correlation potential and including all relativistic effects except the spin-orbital interaction. The correlation, which corresponds to non-spherical terms, is not included [7].

When employing the LMTO-ASA method, there is no need to use equal radii for all atomic spheres or to restrict the sphere positions to the atomic sites. As is seen from the high values of the coordination numbers for copper and aluminium (10 and 15 respectively) the $PtPb_2$ phase with $CuAl_2$-type structure is a rather close packed structure (the packing factor is equal to 0.7) and the LMTO method may give rather good results. The electronic configurations of atomic cores were taken from the atomic configurations and are $1s^2 \ldots 5p^6$ and $1s^2 \ldots 5d^{10}$ for platinum and lead respectively. The configurations of the valence electrons are $5d^9 6s^2$ and $6s^2 6p^2$ for platinum and lead respectively. The primitive unit cell was selected for calculations with $a_p = 4.854$ Å, $c = 5.764$ Å and $Z = 2$ (six atoms).

The calculations were performed for the basis set of angular momenta s, p and d. The band structure was calculated for 30 inequivalent points in the irreducible part of the Brillouin zone. The tetrahedron method was used for the density of states calculation.

The ratio of Wigner–Seitz radii R_{Pt}/R_{Pb} for platinum and lead taken from the atomic radii ratio, was constant and equals 0.792. It is easy to calculate the values of the radii from the equation:

$$a^2 c = (4\pi/3)(2R_{Pt}^3 + 4R_{Pb}^3)$$

$R_{Pt} = 2.79$ u and $R_{Pb} = 3.53$ u at normal pressure.

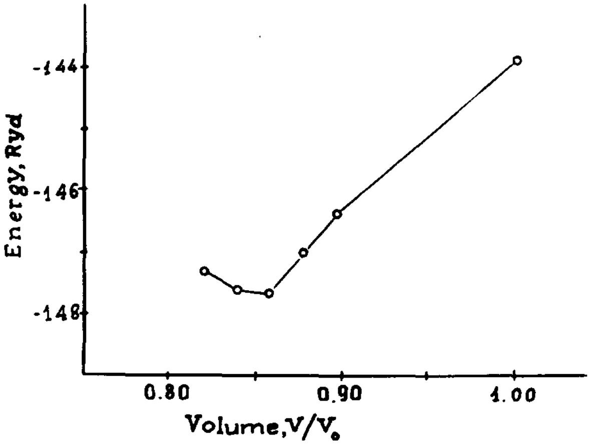

Fig. 1. The volume dependence of the total energy of the new phase $PtPb_2$ ($CuAl_2$ type).

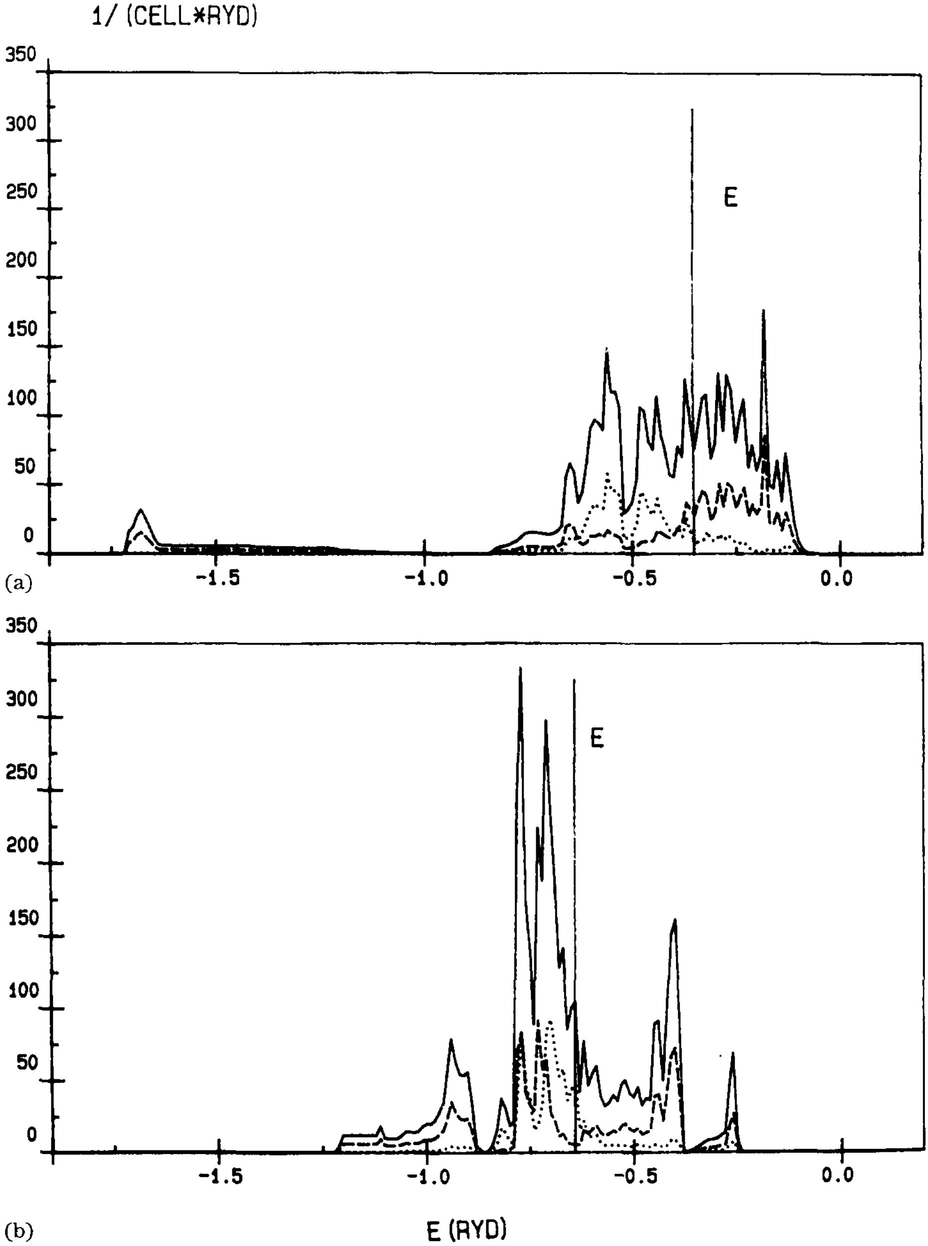

Fig. 2. Density of states for (a) the high pressure phase ($V = 0.86\ V_0$) (b) the phase at normal pressure ($V = V_0$); V_0 is the volume calculated from X-ray data at atmospheric pressure.

The dependence on volume of the total energy is shown in Fig. 1 and the densities of states for the $PtPb_2$ phase at high pressure and at normal pressure are shown in Fig. 2.

5. Discussion

It follows from the experimental results that the $PtPb_2$ phase with the $CuAl_2$-type structure is unstable under standard conditions but has a field of stability at pressures higher than 5 GPa. The theoretical calculations of the volume dependence of the total energy (see Fig. 1) point in the same direction because its minimum corresponds to the volume $V_p \approx 0.86V_0$, where V_0 is the volume measured under normal conditions.

The total density of states calculated for these two values of volume (V_0 for normal pressure and V_p for high pressure) does not differ much (see Fig. 2). It is seen that in the equilibrium state the densities of state for platinum and lead atoms are about the same at the Fermi level. However, the density of states of the lead atoms is about one order of magnitude smaller than that of platinum at normal pressure.

The following explanation may be offered to explain why $PtPb_2$ does not exist under ordinary conditions. The hybridization between lead and platinum electrons is probably fairly small. Only at smaller volumes (*i.e.* at high pressures) does this hybridization become large enough to stabilize the intermetallic compounds. This may be the reason why this phase can be prepared using high pressure techniques. Also it can be retained under standard conditions but it has a very low temperature of decomposition.

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