Synthesis, crystal structure and electronic structure of the binary phase Rh$_2$Cd$_5$

Biplab Koley[a], S. Chatterjee[b], Partha P. Jana[a,*]

[a] Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India
[b] Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

ABSTRACT

A new phase in the Rh-Cd binary system - Rh$_2$Cd$_5$ has been identified and characterized by single crystal X-ray diffraction and Energy dispersive X-ray analysis. The stoichiometric compound Rh$_2$Cd$_5$ crystallizes with a unit cell containing 14 atoms, in the orthorhombic space group *Pbam* (55). The crystal structure of Rh$_2$Cd$_5$ can be described as a defect form of the In$_3$Pd$_5$ structure with ordered vacancies, formed of two 2D atomic layers with the stacking sequence: ABAB. The A type layers consist of (3.6.3.6)-Kagomé nets of Cd atoms while the B type layers consist of (3^5) (3^7)- nets of both Cd and Rh atoms. The stability of this line phase is investigated by first principle electronic structure calculations on the model of ordered Rh$_2$Cd$_5$.

1. Introduction

In recent years, intermetallic compounds have been identified as a possible source for new electronic and catalytic materials. They have richly varied structural chemistry, electronic structures and physical properties. [1–4].

The search for the new Rh-based intermetallics has generated much interest as such compounds have been identified as potential heterogeneous catalysts for chemoselective hydrogenation, electrocatalytic oxidation, and selective isomerisation, etc [5–9]. For instance, Rh-Pd intermetallic compounds have been used for the hydrogenation of p-nitrostyrene to p-aminostyrene and Rh-Sn nanoparticles have the ability to perform electrocatalytic oxidation of ethanol.

Binary transition element bearing Zn or Cd compounds have attracted considerable interests as these compounds show peculiar and intricate structures [10–14] as well as very intriguing chemical and physical properties [15–17]. Among them, rhodium forms several binary intermetallic compounds with Zn in the zinc-rich region such as CsCl type RhZn, γ-brass type Rh$_2$Zn$_{11}$ and CoZn$_{13}$ type monoclinic RhZn$_{13}$ [18]. Zn and Cd are located in the same group in the periodic table and they are isoelectronic. Hence, it is assumed that complete replacement of Zn by Cd in the reported Rh-Zn binary intermetallics may form a number of stable intermetallic phases. Moreover, Westgren et al. indicated (1930) that γ-brass related Rh$_5$Cd$_{11}$ might exist in Rh-Cd binary system. These reports have motivated us to examine the Cd-rich region in the Rh-Cd system [19].

Our recent study on Cd rich part of the Rh-Cd system has uncovered a new line compound with the *c.a.* 29 at% of Rh. The present investigation is aimed at resolving the structure and stability of the line compound Rh$_2$Cd$_5$ in the Rh-Cd binary system. In addition to this, the atomic ordering (site preference of rhodium in the structure of Rh$_2$Cd$_5$) has been confirmed by quantum mechanical first principle total energy calculations.

2. Materials and methods

2.1. Syntheses

The Rh$_2$Cd$_5$ phase was synthesized in a high temperature reaction starting from the pure Rh (99.95% Alfa Aesar) and Cd (99.9999%, Chempur). Samples of precisely weighed metals (approximately 0.3 g each) were loaded and sealed in argon-purged evacuated silica ampoules. The molar fraction x$_{Rh}$ of the mixtures was systematically varied between 0.28 and 0.30. The metal mixtures were heated up to 1173 K at a rate of 194.4 K h^{-1}. The ampoules were kept for 6 h at this temperature. The temperature was subsequently reduced to 623 K over a period of 96 h and the sample was annealed at this temperature for 96 h. Finally, the samples were slowly cooled to room temperature over a period of 12 h. Products formed were silvery, brittle ingots, stable in air.

2.2. X-ray diffraction data collection and processing

Crystals were picked from the crushed ingot, mounted on a glass

Table 1
Crystallographic data for the single crystal structure refinements of Rh_2Cd_5 (C1).

	C1
Crystallographic data	
Chemical formula	Rh_2Cd_5
Chemical formula (%)	$Rh_{28.57}Cd_{71.43}$
EDS formula (%)	$Rh_{28.2(3)}Cd_{71.9(3)}$
Pearson symbol	$op14$
X_{Rh}	0.286
Crystal system	Orthorhombic
Space group type; Z	$Pbam$ (55); 2
a,b,c/Å	a=5.648(1), b=10.607(2), c=4.372(1)
V /Å^3	261.95(8)
ρ_{calcd}/g cm^{-3}	9.7318
μ/mm^{-1}	25.867
Crystal color	silvery with metallic luster
Data collection	
Diffractometer	Four-circle diffractometer, Xcalibur, Eos
Radiation	$Mo_{K\alpha}$
Monochromator	Graphite
T/K	293(2)
θ_{min}–θ_{max}/°	3.6–32.34
Reflns measured	2458
Index range	$-8 \leq h \leq 7$
	$-16 \leq k \leq 15$
	$-6 \leq l \leq 6$
Completeness of data set	0.9980
Absorption correction	multi-scan
Unique reflns	509
R_{int}	0.0333
Structure solution/refinement	*JANA* 2006 package program [20]
Structure solution	Superflip [21]
No. reflns used	509
No. variables	24
Observed reflns (I > 3σ(I))	487
R(F^2 > 3σ(F^2))	0.0166
R(F) (all data)	0.0180
k[a]	0.0004
wR (F^2)(all data)	0.0446
GOF (all)	1.28
$\Delta\rho_{min}/\rho_{max}$/eÅ^{-3}	−1.43/1.21

[a] weighting scheme: w =1/[σ^2(I)+k(I)^2)].

fiber and diffraction intensities were collected with an Oxford Diffraction Xcalibur Eos equipped with MoKα radiation (λ=0.71073 Å, 50 kV, 40 mA) at ambient temperature. Data collection and reduction were performed with the *CrysAlis* package program from Oxford diffraction. The structure solution and the refinement were carried out using the Jana2006 program [20,21]. Data collection and refinement details are given in the Tables 1, 2. Further details can be found in the CIF file deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de.

Powder diffraction data for Rh_2Cd_5 were collected by a STOE STADIP diffractometer (CuK$_{\alpha1}$=1.5406 Å, 40 kV, 40 mA).

2.3. Energy dispersive X-ray analysis

The composition of selected specimens was examined in a scanning electron microscope (a JEOL 3000 with a secondary electron (SEI)

Table 2
Structural data for Rh_2Cd_5 (C1).

Site	Atom	Wyck	SOF	x/a	y/b	z/c	Ueq[a][Å^2]
M1	Cd1	2c	1	0	½	0	0.01013(15)
M2	Cd2	4g	1	0.39625(7)	0.27774(4)	0	0.00949(11)
M3	Cd3	4h	1	0.16373(7)	0.09691(4)	1/2	0.00970(11)
M4	Rh4	4h	1	0.13999(7)	0.35467(4)	1/2	0.00798(12)

detector) equipped with an energy dispersive X-ray spectrometer (EDS).

2.4. Electronic structure calculations

To understand the stability of the ordered model compound-Rh_2Cd_5, the refined crystallographic results from X-ray diffraction data have been used to perform electronic structure calculation using density functional theory (DFT) [22,23] within the framework of local-density approximation (LDA) as well as generalized gradient approximation (GGA). For our DFT calculations we considered a combination of two different methods, namely, muffin-tin orbital (MTO) based linear muffin-tin orbital LMTO method as implemented in Stuttgart TBLMTO-47 code [24–27] and a plane-wave-based method as implemented in the Vienna ab initio Simulation Package (VASP).

For our LMTO calculations, exchange and correlation were treated according to *von Barth-* and *Hedin* local density approximation. [28] All relativistic effects except spin-orbit coupling were taken into account by using a scalar relativistic approximation. [29] In ASA (atomic sphere approximation), space is filled with small, overlapping Wigner–Seitz (WS) spheres at each atomic site. The symmetry of the potential is considered to be spherical inside each WS sphere, and a combined correction takes the overlapping part into account. The radii of the WS spheres were optimized under the requirement that the overlapping potential should give the best possible approximation to the full potential by an automatic procedure. [30] For Rh_2Cd_5, the basis set included Cd: *5s, 5p* and *4d* orbitals and Rh: *5s, 5p* and *4d* orbitals. The Brillouin zone integrations were accomplished on a 9×9×9 k-point mesh with the tetrahedron method. [31] For the plane wave based calculations, projector augmented wave (PAW) [32,33] method as implemented in the plane-wave based VASP code [34–36] was employed. Both local-density-approximation (LDA) and (PBE) [37] implementation of the generalized gradient approximation (GGA) exchange correlation functional have been used and the results found are consistent. The reciprocal space integration was carried out with a k mesh of 12×6×12. The atomic positions have been optimized using the conjugate-gradient algorithm [38], by keeping the lattice constants fixed at the experimentally estimated values, until the Helmann-Feynman forces [39] became less than 0.005. We have also cross-checked our results by allowing for the full optimization of the lattice and found the results to be consistent. The energy convergence with respect to various computational parameters was carefully examined.

VASP was employed to address the "coloring problem" [40]. The stability analysis of the structures from the total energies of the three different model structures of Rh_2Cd_5 and their corresponding density of states (DOS) were calculated from VASP. Our analysis was further strengthened from the results of the COHP calculations performed using LMTO package.

3. Results

3.1. Structural solution, refinement and phase analysis

The structure of the newly found compound was solved in the space group *Pbam* (55). Four atomic positions were generated after an initial structural solution (M1 (2c), M2 (4g), M3 (4h), M4 (4h)). A preliminary cycle of refinement converged at the R(F^2) value somewhat higher than 0.05. In the Rh-Cd binary system, it was not straight forward to assign all atomic sites based on electron density only, due to the similarity between the cadmium (Z=48) and rhodium (Z=45) scattering factors. As the phase is presumed cadmium rich from the preparative method, all the atomic position (M1, M2, M3, M4) at first were assigned to cadmium, and the refinement led to the residual factor of R(F^2) =0.049. At this stage, thermal displacement parameters of four positions were carefully analyzed. Three atomic positions (M1,