	Experiment title: High pressure studies on complex intermetallic compounds	**Experiment number**: 01-02-722
Beamline: BM01A	**Date of experiment**: from: 2005-10-30 to: 2005-11-1	**Date of report**: 2006-01-25
Shifts: 6	**Local contact(s)**: Vladimir Dmitriev	*Received at ESRF:*

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Report:

According to Urban & Feuerbacher, complex intermetallic compounds are 'exceptional metallic systems based on crystal structures with giant unit cells comprising up to more than a thousand atoms per unit cell' (J. Non-Cryst. Solids (2004) **334&335** 143). Because of the complexity of their structures and the different length-scales present in the structures due to the large unit cells, interesting physical properties may occur. With these measurements, a feasibility study was performed on the 'amount of complexity' that can be handled with X-ray powder measurements using a diamond-anvil cell. The compounds $PdGa_5$, Rh_3Bi_{14}, and $Rh_3Bi_{12}Br_2$ were chosen, because they show interesting chemical bonding as well as a different degree of structural complexity. The unit cell volume at zero pressure is given in table 1. Rh_3Bi_{14} and $Rh_3Bi_{12}Br_2$ are isostructural and built up of a Rh-Bi framework with channels, either filled with Bi- or Br-atomes. The stability and bonding as a function of pressure is therefore of special interest.

Powder diffraction measurements were performed on $PdGa_5$, Rh_3Bi_{14}, and $Rh_3Bi_{12}Br_2$ up to 40.4, 30.6, and 32.6 GPa, respectively, on the marIP using an ETH diamond anvil cell (DAC) at a wavelength of 0.7093 Å. To minimize the unwanted scattering of the gasket, the beam diameter was reduced to about 80×80 μm^2 using the slits of the mar-stage. The SNBL system for cell alignment was used, which improved the alignment process and obtainable data quality very much. In figure 1 representative powder patterns of the three compounds at various pressures are shown. Unfortunately, data collected from $PdGa_5$ using a heatable Diacell diamond-anvil cell up to ca. 32 GPa and 300 °C was not usable due to too weak intensities of sample reflections caused by alignment problems.

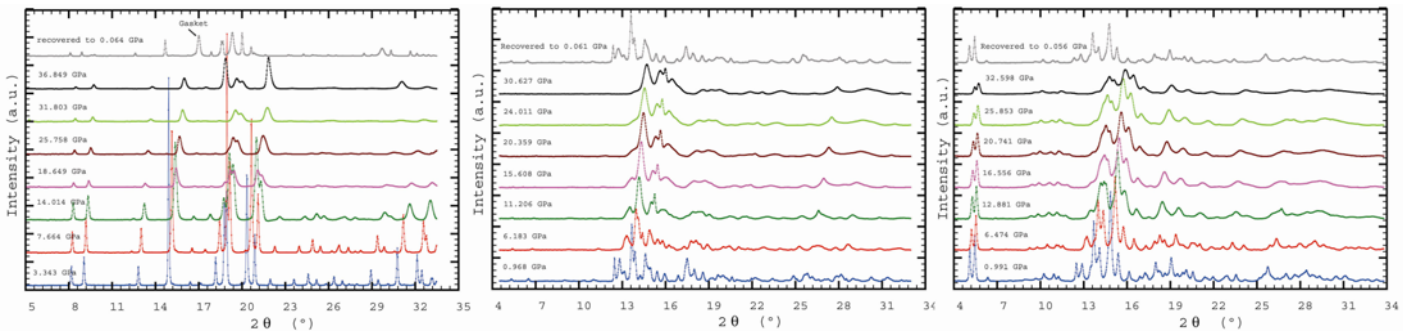

Figure 1. Representative powder diffraction patterns of $PdGa_5$, Rh_3Bi_{14}, and $Rh_3Bi_{12}Br_2$ (from left to right)

Rietveld refinements were performed by the use of the Fullprof and GSAS program packages. For $PdGa_5$ structural refinements were possible, but in the case of the more complex Bi-compounds, structural refinements were not possible due to the peak broadening at higher pressures and severe peak-overlapping.

Up to 40.4 GPa, all the diffraction patterns of $PdGa_5$ correspond to the ambient pressure phase, indicating that $PdGa_5$ is stable within the applied pressure range at room temperature. Rh_3Bi_{14} and $Rh_3Bi_{12}Br_2$ were studied up to 30.6 and 32.6 GPa. All the diffraction patterns of Rh_3Bi_{14}, $Rh_3Bi_{12}Br_2$ correspond to their ambient pressure phases, indicating that both compounds are stable in the experimental pressure range at room temperature. Figure 2 shows third-order Birch-Murnaghan equations of state fitted to the experimental data. The zero-pressure volume V_0, the zero-pressure bulk modulus K_0 and its presssure derivative K' is derived for the compounds as summarized in table 1.

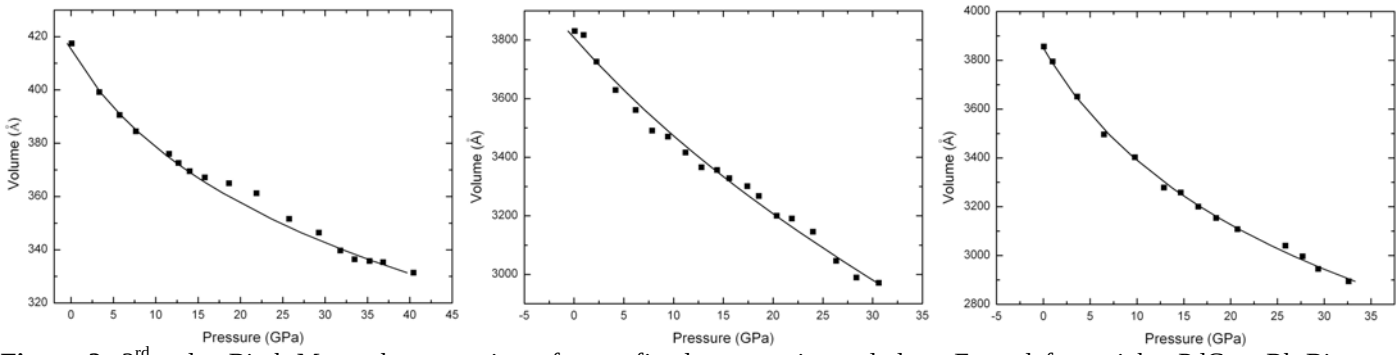

Figure 2. 3rd-order Birch-Murnaghan equation of state fitted to experimental data. From left to right: $PdGa_5$, Rh_3Bi_{14}, and $Rh_3Bi_{12}Br_2$.

Table 1. Zero pressure volume V_0, zero-pressure bulk modulus K_0 and its pressure derivative K' for the studied compounds

	V_0 (Å)	K_0 (GPa)	K'
$PdGa_5$	414.96	76.6±5	7.8±1.4
Rh_3Bi_{14}	3807.27	99.1±8.2	2.2±0.4
$Rh_3Bi_{12}Br_2$	3850.14	57.03±6.9	5.0±0.7

In order to understand the stabilization and characterize the chemical bonding, quantum chemical calculations were performed by the use of the Vienna ab initio simulation package (VASP) and the projector augmented wave (PAW) method. The calculations of geometry optimization and phase stability were performed by means of the generalized gradient approximation (GGA) based on the density functional theory (DFT). The results were analyzed using the Electron Localization Function of the valence electrons (ELFV). Figure 3 shows representative ELF images of the studied complex intermetallic compounds. $PdGa_5$ shows strong covalent Ga-Ga bonds. The "empty space" in the structure remains filled with localized electrons – a pressure up to 40 GPa is not high enough to break the strong covalent bonding. This may be a possible reason for the stability of the structure, although pure Ga is soft and melts at low pressure. For the Rh-compounds a detailed analysis of the electronic properties and ELF topography by use of the TB-LMTO-ASA program package is still in progress.

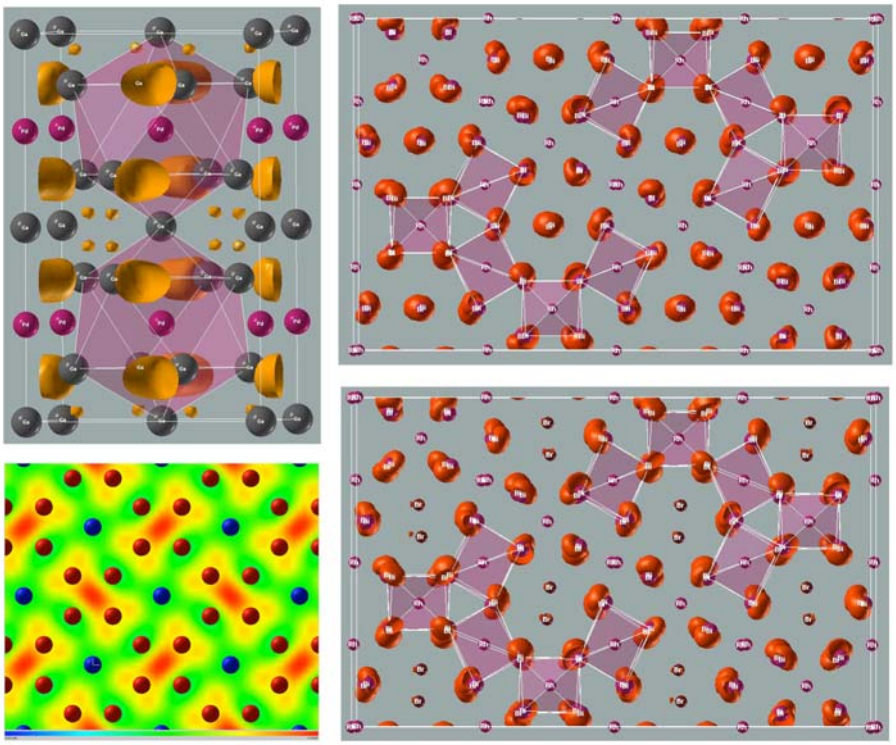

Figure 3. ELFV isosurface plots of $PdGa_5$ (upper left), Rh_3Bi_{14} (upper right), $Rh_3Bi_{12}Br_2$ (lower right). ELFV cut through Ga-Ga bonds (Ga-atoms are shown in red) in $PdGa_5$(lower left).