Electronic topological transition in AuX$_2$ (X = In, Ga and Al) compounds at high pressures

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S K Sikka**[1]**, V Vijayakumar**[1]**, A Lausi**[2] **and E Bussetto**[2]

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Abstract

We present accurate x-ray diffraction data at high pressures for AuIn$_2$, AuGa$_2$ and AuAl$_2$, obtained using a diamond anvil cell with the ELETTRA synchrotron source. The resulting P–V data obtained from the d-values were used to get the universal equation of state (UEOS), which is compared with theoretical estimates. Deviation from linearity is evident in the UEOS curves of AuIn$_2$ and AuGa$_2$, thus verifying that some of the observed anomalies in these systems below 5 GPa are due to electronic topological transitions.

Gold forms intermetallic compounds of the CaF$_2$ structure [1]. These are known to exhibit low residual resistivities. The bright mauve colour of AuAl$_2$, as opposed to the bluish shade of AuIn$_2$ and the neutral appearance of AuGa$_2$, is consistent with the observed differences in their optical transitions and band structure [2]. There are other differences concerning the anomalous Knight shift of Ga in the AuGa$_2$ compound compared to the normal behaviour of Al and In in the other two compounds and the different thermoelectric behaviour of AuGa$_2$ [3]. However, other measurements (e.g. of the specific heat [4] and Hall coefficient [3]) do not indicate any significant difference in these compounds. Storm *et al* [5] studied the fusion behaviour of these compounds up to pressure of 5 GPa. Their measurements showed that the fusion curve of AuAl$_2$ decreases while those of AuGa$_2$ and AuIn$_2$ change slopes, suggesting possible phase changes. Variation of the thermoelectric power with pressure showed anomalies for AuIn$_2$ and AuGa$_2$ near the pressures at which fusion anomalies occurred. Observation of these anomalies motivated various high-pressure studies of their electrical and structural behaviour [6, 7]. Also first-principles band structure calculations were carried out which attributed them to electronic topological transitions (ETT) in AuIn$_2$ and AuGa$_2$ at the pressure values where the fusion and thermoelectric power measurements showed anomalies and indicated no trace of such transitions in AuAl$_2$. It has been pointed out that precise P–V equation of state (EOS) obtained either experimentally or theoretically when transformed to a universal equation of state (UEOS) [8] can reveal signatures of electronic transitions through deviation from linearity. In the present case the first-principles theoretical calculations carried out by us using full-potential
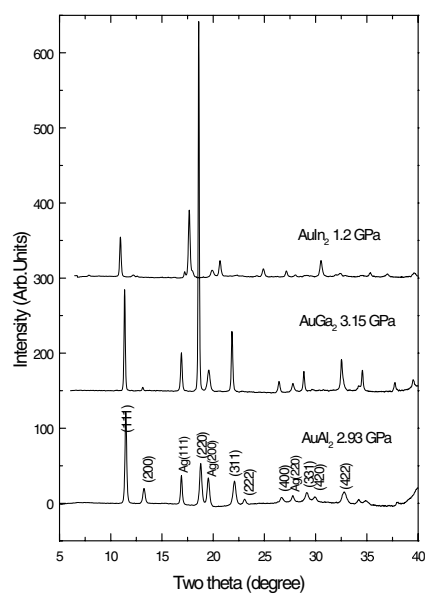
Figure 1. X-ray diffraction patterns of AuIn$_2$, AuGa$_2$, and AuAl$_2$ at ambient pressure.
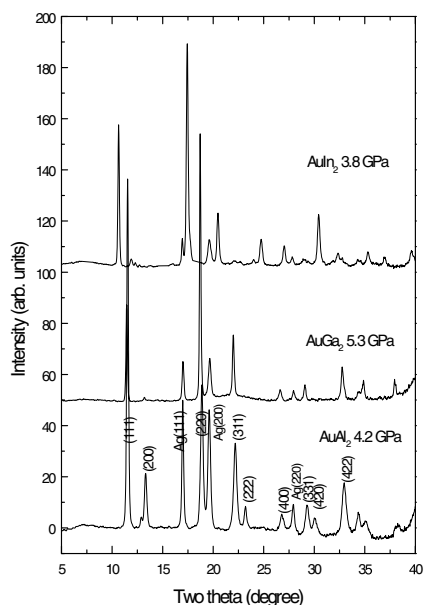

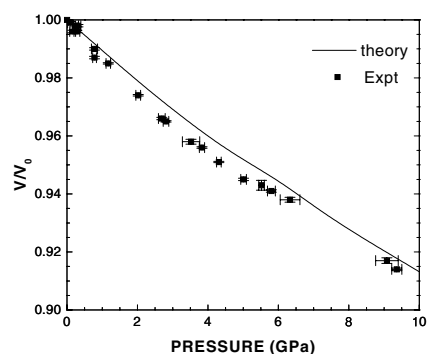**Figure 2.** X-ray diffraction patterns of AuIn$_2$, AuGa$_2$, and AuAl$_2$ around 5 GPa.

Figure 3. The equation of state for AuIn$_2$.

energy band structure methods revealed deviation from linearity in AuIn$_2$ and AuGa$_2$ but not in AuAl$_2$. The aim of the present experimental studies was to confirm these theoretical findings using high-precision synchrotron data at high pressure.

High-pressure x-ray diffraction measurements were carried out using the synchrotron radiation source at ELETTRA, Trieste, Italy. Clamp-type Merrill–Bassett and Mao–Bell cells fabricated by us were employed in these experiments [9]. Fine particles of AuIn$_2$ were loaded
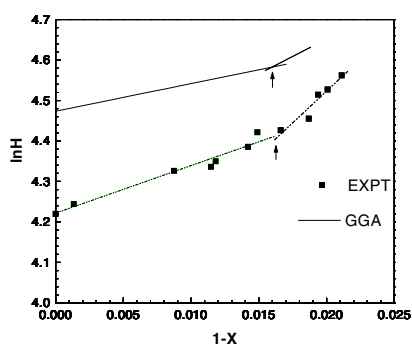
Figure 4. The experimental UEOS for AuIn$_2$ as compared to that obtained by theoretical estimates, showing good agreement for the anomaly.
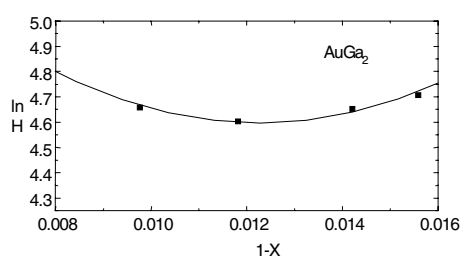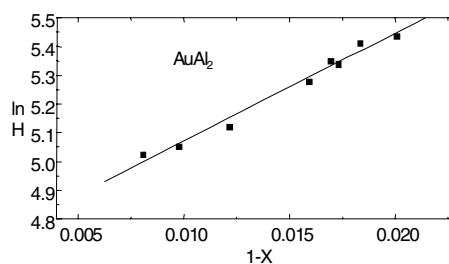

Figure 5. The experimental UEOS for AuGa$_2$.

Figure 6. The experimental UEOS for AuAl$_2$.

into a hardened stainless steel gasket hole of 150 μm diameter along with silver as the internal pressure marker. Ethanol was used as the pressure-transmitting medium. The ELETTRA diffraction beamline has been designed to provide a monochromatized high-flux tunable x-ray source in the spectral range between 4 and 25 keV [10]. The radiation source is the 57-pole wiggler. The experimental station is based on a 345 mm imaging plate (IP) area detector from Mar Research. The sample-to-IP distance was calibrated by collecting data for silver. The x-ray wavelength used was 0.690 Å. The data were collected up to 20 GPa with a typical exposure time of 15 min at each pressure. The scanned two-dimensional diffraction patterns were corrected for tilt and scanner distortions and converted to intensity versus 2θ through radial integration using our own software package and public-domain software [11]. The precision in the d-values obtained using the ELETTRA synchrotron was higher by almost a factor of 2 compared to that obtained with a laboratory (rotating-anode generator) x-ray source. With this higher accuracy, it is now possible for us to verify the UEOS predicted by theoretical calculations.

The experiment was repeated for AuGa$_2$ and AuAl$_2$ samples. The evolutions of the diffraction patterns at the lowest pressure available for all three intermetallics are shown in figure 1; the peaks could be indexed to the ambient phase CaF$_2$ cubic structure (space group $Fm3m$). Figure 2 shows the diffraction patterns for all three compounds at around 5 GPa pressure; it shows that all of them maintain the CaF$_2$ structure. As the anomalies observed in these intermetallics occur below 5 GPa, the data of figure 2 show that a structural transition is not responsible for the anomalies discussed above, and supports the view that the anomalies are due to electronic structure changes under pressure.

The UEOS as given by Rose *et al* [8] is as follows:

$$\ln H = \ln[PX^2/3(1-X)] = \ln K_0 + \eta(1-X),$$

where $X = (V/V_0)^{1/3}$, P is the pressure, V_0 is the normal volume, and η is related to K_0' (the pressure derivative of the bulk modulus) by

$$\eta = 3(K_0' - 1)/2.$$

Hence we obtained an accurate $P–V$ curve (figure 3) from the measured d-values and checked through the use of UEOS for the signatures of the electronic anomaly suggested earlier [6].

As observed from figure 4 there is indeed a change of slope at 3.8 GPa in $AuIn_2$, which agrees well with the estimates of theoretical calculations, although no significant structure is seen in the experimental and theoretical $P–V$ curves. Figure 5 shows the UEOS for $AuGa_2$, which has only four observed points, but they match very well with the theoretical findings [7] which shows two linear branches. Figure 6 shows the UEOS for $AuAl_2$ and in this case no deviation from linearity is seen.

In conclusion, we can state that accurate measurements employing a synchrotron source support our earlier theoretical interpretation that the anomalies observed below 5 GPa pressure in $AuIn_2$ and $AuGa_2$ are due to an ETT and confirms that there is no such transition in $AuAl_2$.

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[8] For example, for demonstrating the deviation of the universal equation of state (UEOS) from linearity as a result of such electronic transitions, see
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