A.11: High pressure studies on $FeGa_3$

Intermetallic systems are known for their technologically important properties and the rich underlying physics. Although a vast majority of intermetallics are metals, there are a few semiconductor intermetallic systems also. The values of the bandgap in these intermetallic semiconductors strongly depend upon the nature of hybridization between the orbitals of the constituent atoms. A few intermetallic compounds, which are reported to have a band gap, include FeSi, FeSb, RuAl, $FeGa_3$, $RuGa_3$ and RuIn. These are considered to be promising materials for applications in infrared and thermal devices due to their low bandgap and the presence of large density of states at the valence band edge. Among the transition metal (TM) based narrow bandgap semiconductors, $FeGa_3$ is one of the most well studied materials. Band gap of this material is reported, from experiments, to be in the range of 0.3–0.5 eV. First-principles based electronic structure calculations with local density approximation (LDA) and generalized gradient approximation (GGA) give similar values for the band gap.

Although geometric, electronic and magnetic, properties of $FeGa_3$ at ambient conditions are reported in the literature, there are no experimental studies on the properties of this material under high pressure. To the best of our knowledge, there is only one report on the computational study on the high-pressure properties of $FeGa_3$, which predicts that $FeGa_3$ undergoes a semiconductor to metal transition at ~25 GPa. The application of external pressure provides a very useful means to modify the nature of bonding and hybridization strength between Fe 3d and Ga 4s and 4p orbitals, resulting in changes in unit cell volume, electronic and magnetic properties, without introducing any extra chemical element, charge carriers or defects.

Polycrystalline samples made by induction melting were studied at the Extreme conditions XRD beam line (BL-11, Indus-2) in collaboration with High pressure and Synchrotron Radiation Physics Divn. (BARC). Pressure was applied using a Mao-bell type pressure cell using Au as the pressure indicator and Methanol-ethanol (4:1) mixture as the pressure transmitting medium. Density functional theory (DFT) based electronic structure calculations, with the GGA exchange-correlation functional, have been performed using Vienna *ab-initio* simulation package (VASP). In order to probe the effect of strong-correlation, if any present in the system, we have also carried out the calculations using GGA+ U method.

The variation of the XRD pattern with pressure is shown in Figure A.11.1(a). Figure A.11.1(b) shows the derived equation of state (EOS) of $FeGa_3$ from experiments and the calculated values of volume of the unit cell as a function of pressure. We have observed that the GGA calculation underestimates the unit cell volume, and this difference increases with applied pressure. The calculated values of unit cell volume vs. applied pressures for different *U* values (where *U* is the on-site Coulomb repulsion between the Fe 3d electrons) are also shown in Figure A.11.1(b). A good match between the experiments and the calculations could only be achieved by increasing the values of *U* with pressure.

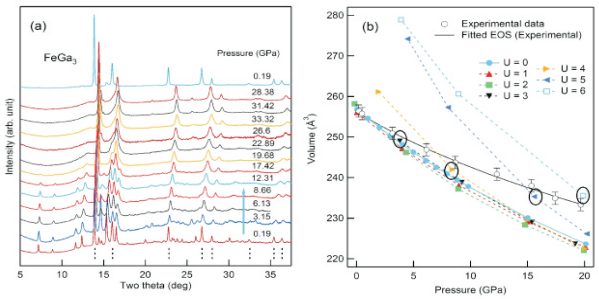

Fig. A.11.1: (a) XRD data as a function of pressure (b) fitting of EOS with calculation.

To find out the evolution of electronic structure of $FeGa_3$ with pressure, total density of states (DOS) and the partial DOS of 3d electrons of Fe have been calculated with different *U* values that were required to reproduce the experimental volume at different pressure. We can clearly observe that the system undergoes an insulator to a metal transition at ~ 4 GPa and also becomes magnetic beyond this pressure.

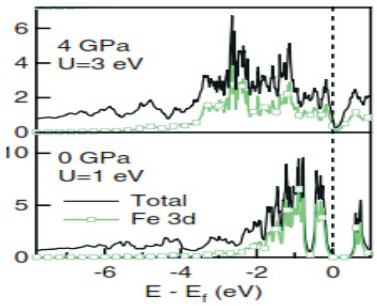

Fig. A.11.2: Calculated electronic density of states with pressure showing the gap closing with pressure.

Electronic structure calculations show that around a pressure of 4 GPa a small finite DOS arise at the Fermi level (see Figure A.11.2), and a signature of this phenomenon has been observed in pressure dependent resistance measurements as well carried out at High Pressure and Synchrotron Radiation Physics Division of BARC. To conclude, we have established the important role of on-site Coulomb repulsion between the Fe 3d electrons on the structural and electronic properties of $FeGa_3$ at high pressure. For details please refer: *Debashis Mondal et al., Phys. Rev. B, 95, 134105 (2017)*

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