

Striking Effect of Pressure and Temperature on PdSe₂ Allotropes

Céline Sortais-Soulard^{a,b}, S. Jobic^b, W. Crichton^c, ^aCEA/DPTA, BP12, 91680 Bruyères le Châtel, France. ^bIMN, 2 rue de la houssinière, 44000 Nantes, France. ^cESRF, BP 220, 38043 Grenoble Cedex. E-mail: celine.sortais@cea.fr

Under ambient conditions, PdSe₂ adopts the PdS₂-type structure (o-PdSe₂). Its crystal structure at high pressure (up to 30 GPa) was investigated at 20°C and at 300°C by X-ray energy-dispersive diffraction. Le Bail refinements and *ab initio* calculations evidenced a solid-solid phase transition to the pyrite-type structure (c-PdSe₂), strongly related to the o-PdS₂. Using the experimental data obtained at 20°C and 300°C, we examined the order of the PdSe₂ phase transition and its dependence on temperature. For this purpose, we calculated and analyzed the thermodynamical potential and the entropy generation by numerically calculating the equation of state.

We also found that the cell volume of c-PdSe₂ was smaller at 300°C than at 20°C by nearly 40%. Such a dramatic decrease in the unit cell volume meant a strong reorganization of the bonding and was suggestive of an incoming phase transition. This possibility has been experimentally confirmed by fledgling high pressure experiments at ESRF. We surprisingly found that the new allotropic phase was a 2D CdI₂-type structure. It probed that all MSe₂ (M=transition metal) structures are linked. We evidenced the interconversion path between the 3 allotropes, explaining their relative stabilities on the basis of a thermodynamic and electronic structure study.

Keywords: phase transitions in solids, thermodynamics, x-ray synchrotron powder diffraction