Raman/x-ray-diffraction/*ab-initio* study of cubic $Zn_{1-x}Cd_xSe$ ($x \leq 0.3$) at ambient and high pressure

M.B. Shoker,[1] O. Pagès,[1,*] H. Dicko,[1] A. Polian,[2] A.V. Postnikov,[1] V.J.B. Torres,[3] F. Firszt,[4] K. Strzałkowski,[4] A. EnNaciri,[1] L. Broch,[1] A. Maillard[5] and J.-P. Itié[6]

[1] *LCP-A2MC, Institut Jean Barriol, Université de Lorraine, Metz F-57078, France*
[2] *IMPMC, UMPC, UMR CNRS 7590, Sorbonne Université, F-75005 Paris, France*
[3] *Departamento de Fisica and I3N, Universidade de Aveiro, 3810 – 193 Aveiro, Portugal*
[4] *Institute of Physics, N. Copernicus University, 87-100 Toruń, Poland*
[5] *LMOPS, Institut Jean Lamour, Sup'Elec, Université de Lorraine, Metz, F-57078, France*
[6] *Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 F-91192 Gif-sur-Yvette Cedex, France*

* Corresponding author: olivier.pages@univ-lorraine.fr

The $Cd_xZn_{1-x}Se$ mixed crystal was long believed to exhibit the rare 1-phonon mode behavior in its Raman spectra,[1] essentially due to its longitudinal optic (LO) mode(s). However, the picture has been challenged over the past two decades in view of far-infrared reflectivity spectra revealing a fine structure behind the presumed unique transverse optic (TO) mode, echoed by LO replicas.[2] In this work we further examine the phonon mode behavior of $Cd_xZn_{1-x}Se$, which remains an issue, by performing a pure-TO Raman study concerned with zincblende-type single crystals ($x \leq 0.3$). Both the phonon-polaritons equipped with a photon-like electric field near Γ (q~0) and their native purely-mechanical variants away from Γ are covered using suitable near-forward and backward scattering geometries, respectively.

The (TO) fine structure is described in terms of a $[1 \times (Cd-Se), 2 \times (Zn-Se)]$ three-phonon percolation-type pattern,[3] in which the Cd-Se vibration is blind to its local environment and the Zn-Se doublet distinguishes between vibrations in the like (ZnSe) and foreign (CdSe) environments (as defined at the next-nearest-neighbor scale). Apparent anomalies, i.e., the quasi TO-LO degeneracy (in fact, an inverted one) of the CdSe-like Zn-Se mode, which goes with its abnormally (TO) Raman intensity, are attributed to a trend towards local clustering, leading to a massive transfer of oscillator strength between the two Zn-Se modes. To our view the local clustering is a precursor sign of the approaching composition-induced zincblende→wurtzite structural transition at x=0.3. The amount of clustering is estimated by working out a zincblende version of the percolation scheme equipped with a relevant order parameter.

Next, we extend the $Cd_xZn_{1-x}Se$ ($x \leq 0.3$) Raman study at high pressure up to the zincblende→rocksalt structural transition (at ~12 GPa), using a diamond anvil cell. Our ambition is to use the Zn-Se percolation doublet as a *sensitive probe at the mesoscopic scale* to investigate how the Zn-Se bonds engage the pressure-induced structural phase transition depending on whether they vibrate in their like (ZnSe) or foreign (CdSe) environments. Similar studies have been done earlier with the alternative ZnSe-based $Zn_{1-x}Be_xSe$ and $ZnSe_{1-x}S_x$ percolation-type systems,[4,5] with this difference, though, that in the latter cases the percolation doublet (of the Be-Se or Zn-S types) did relate to the minor bond species, and not to the dominant (Zn-Se) one as in the present case. With $Zn_{1-x}Be_xSe$ and $ZnSe_{1-x}S_x$ we concluded to a phonon-freezing of the minor bonds vibrating in their like/minor environment on approach to the pressure-induced structural transition. Such phonon-freezing is not realistic for the dominant Zn-Se bond of $Cd_xZn_{1-x}Se$ vibrating in its like environment, as it would be concerned with the entire host medium. The minor Zn-Se bonds vibrating close to Cd, i.e., in the foreign/minor (CdSe) environment, are presumably more prone to phonon-freezing, which we presently investigate using both experiment and theory.

The Raman study is supported by (high-pressure) x-ray diffraction measurements done at the PSICHÉ beamline of the synchrotron SOLEIL and by (high-presure) *ab initio* calculations on large (Zn,Cd)Se supercells (containing up to ~200 atoms) as concerned with (i) the limit vibrations of the three phonon branches at both ends of the composition domain (x~0,1) using prototypical impurity motifs and with (ii) the actual Raman spectra at intermediary composition (x~ 0.4).

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