$Zn_{1-x}Mn_xTe$ & $Zn_{1-x}Be_xSe$
High-pressure lattice structure/dynamics

M. MINA (Université de Lorraine, LCP-A2MC, ER 4632, F-57000 Metz, France),
J. BULLED (European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France),
A. ELMAHJOUBI (Laboratoire Léon Brillouin, UM12 CEA-CNRS, Bât. 563 site de Saclay, 91191, Gif-sur-Yvette, France)
A. POSTNIKOV (Université de Lorraine, LCP-A2MC, ER 4632, F-57000 Metz, France),
A. POLIAN (Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université, CNRS 7590, Paris 75005, France),
M. DE BOISSIEU (SIMaP, Grenoble-INP, UJF, CNRS, 1130 Rue de la piscine, BP 75, 38402 Saint Martin d'Hères Cedex, France),
A. BOSSAK (European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France,
A. IVANOV (Institut Laue-Langevin, ILL, 71 Avenue des Martyrs, Grenoble, 38042, France),
P. BOURGES (Laboratoire Léon Brillouin, UM12 CEA-CNRS, Bât. 563 site de Saclay, 91191, Gif-sur-Yvette, France),
F. BOURDAROT (Université Grenoble Alpes, CEA, IRIG, MEM, MDN, F-38000 Grenoble, France),
N. BINISKOS (Université Grenoble Alpes, CEA, IRIG, MEM, MDN, F-38000 Grenoble, France),
J.P. ITIÉ (Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192, Gif-sur-Yvette, France)
Y. LE GODEC (Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université, CNRS 7590, Paris 75005, France),
K. STRZALKOWSKI (Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, 87-100, Poland),
O. PAGES (Université de Lorraine, LCP-A2MC, ER 4632, F-57000 Metz, France)

Abstract

Due to their simplicity (two chemical bonds arranged at random on a high-symmetry lattice), the pseudo-binary cubic (zincblende-type) $A_{1-x}B_xC$ disordered semiconductor alloys set a benchmark to explore how the lattice is distorted by mixing crystals, as needed to accommodate locally the difference in A-C and B-C bond lengths. The lattice dynamics offers the possibility to address the raised issue at all length scales since the wavelength (λ) of lattice vibrations ranges from quasi infinite, "averaging" over the alloy disorder, for the phonon-photon coupled modes called phonon-polaritons that propagate near the Brillouin zone center (BZC), all the way down to ultimately small wavelengths nearly matching the lattice constant a, "zooming" into the alloy disorder, achieved by phonons near the Brillouin zone boundary (BZB). Further, the optical (O) modes, reflecting an effective bond-stretching, potentially offer a more local (bond-related) insight into the lattice distortion induced by alloying than the acoustic (A) modes, the genuine collective modes of the crystal conveying all bond species into the same dynamics, *i.e.*, at the same frequency, hence providing a macroscopic (bond-collective) insight into the alloy disorder. Experimentally, the phonon-polariton dispersion near the BZC $(\lambda \rightarrow 10^4 \times a)$ and the phonon dispersion across the Brillouin zone $(10^2 \times a > \lambda > a)$ can be measured by forward inelastic light (Raman) scattering (RS, schematically operated in "transmission") and by inelastic neutron (INS, nuclear reactor) or x-ray (IXS, synchrotron) scattering using national facilities, as specified in brackets.

Two "extreme" II-VI alloys are considered, *i.e.*, the well-matched $Zn_{1-x}Mn_xTe$ $(\Delta a/a \sim 3.8\%)$ and highly-mismatched $Zn_{1-x}Be_xSe$ $(\Delta a/a \sim 9.4\%)$ ones, subject to minimum and maximum lattice distortions, respectively.

$Zn_{1-x}Mn_xTe$: Two compositions (x= 0.12, 0.37) situated on each side of the Mn-Te bond percolation threshold[1] (x_c ~0.19, corresponding to the first self-connection of the minor Mn-Te bonds into a pseudo-infinite treelike chain across the crystal, a purely statistical effect of the random Zn↔Mn substitution) are studied at large length scale by combining high-pressure X-ray diffraction (HP-XRD, PSICHÉ beamline – synchrotron SOLEIL) and near-forward-RS. The bulk modulus B_0 obtained by fitting the pressure dependence of the unit-cell volume (a^3) via a Birch–Murnaghan equation of state suffers a major drop below linearity on crossing x_c, below both parent values. This suggests a dramatic lattice fragilization from this limit onwards (to be further documented/studied). Besides, the dramatic dispersion of the phonon-polariton regime probed by forward-RS $(\lambda \rightarrow \infty)$ unveils a dual fine structure behind the ZnTe-like O-mode at both studied x values, distinguishing *homo* (Zn-like) from *hetero* (Mn-like) local environments, as explained by the percolation model.[2] The O-duo is hardly visible in the phonon regime, whether probed near the BZC in backward-RS or near the BZB at ultimately small λ "zooming" into the alloy disorder by INS (IN22 beamline – ILL). Hence, even though $Zn_{1-x}Mn_xTe$ is well-matched, it suffers an effective lattice distortion, evidenced both at large (HP-XRD) and short (*homo* vs. *hetero* local bond environments) length scales.

$Zn_{1-x}Be_xSe$: The large lattice distortion gives rise to a distinct percolation-type Be-Se O-duo (split by ~40 cm^{-1}) already visible in the phonon regime probed by conventional backward-RS near the BZC at large λ "averaging" over the alloy disorder $(\lambda \sim 10^2 \times a)$. Under pressure, the Raman O-duo converges, until crossing at the critical pressure $P_c \sim 14\ GPa$.[3] Beyond P_c, only the upper (*hetero*) O-submode survives, the lower (*homo*) O-submode is quenched, independently verified by *ab initio* phonon calculations using the SIESTA code. The trend is reversible in the downstroke. The quenching was explained and modeled within a concept of a phonon exceptional point being achieved at the resonance/crossing.[4] Not surprisingly, the Be-Se O-duo clarifies (further splits) at ultimately small λ "zooming" into the alloy disorder near the BZB, as observed by INS (IN8 beamline, ILL).[5] The BZB is thus most suitable to investigate whether the percolation model worked out for the *bond-specific* O-modes of semiconductor alloys is echoed, or not, in the, *a priori* less discriminating, *bond-collective* A-modes. High-pressure IXS has recently been done in this line on $Zn_{1-x}Be_xSe$ (ID28 beamline, ESRF) at maximum alloying (x~0.5) across the BZ. The studied A-mode consists of a unique well-defined feature near the BZC, but dramatically broadens halfway the dispersion and eventually splits into a distinct A-duo near the BZB. Further, the upper A-submode is quenched above P_c. The trend is reversible in the downstroke. Altogether, the A-duo strongly reminds of the O-duo.

References: [1]Stauffer & Aharony, Introduction to Percolation Theory, Chap. 2 (Taylor and Francis, Bristol, 1994); [2]Alhaddad *et al., Sci. Rep.* **15**, 1212 (2025); [3]Pradhan *et al., Phys. Rev. B* **81**, 115207 (2010); [4]Shoker *et al., Sci. Rep.* **10**, 19803 (2020); [5]Rao *et al., Phys. Rev. B* **89**, 155201 (2014)