Experimental report

07/03/2025

Proposal: 7-01-598 **Council:** 4/2023

Title: Percolation scenario for hexagonalsemiconductor alloys : A test caseby applying inelastic neutron scattering to wurtzite-Zn0.67Mg0.33S

Research area: Physics

This proposal is a resubmission of 7-01-576

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Samples: Zn0.67Mg0.33S

Instrument	Requested days	Allocated days	From	To
IN8	7	8	13/09/2023	19/09/2023
			25/03/2024	27/03/2024
IN22	7	0		
IN20	7	0		

Abstract:

The A1-xBxC semiconductor alloys are like geometrical objects and thus ideal to study experimentally the A¿B substitution, which relates to the percolation theory. For doing so one needs a local probe, such as the bond force constant (k) addressed by vibrational spectroscopies. Our pioneering studies of the phonon and phonon-polariton dispersions of cubic-Zn1 xBexSe combining inelastic neutron (INS) and light (Raman, RS) scattering revealed a k-sensitivity to the local (A- or B-like) environment across the Brillouin zone. This was formalized via our percolation model (PM) deviating from the historical MREI (modified random element isodisplacement) model, by construction blind to the local environment. Our aim in this work is to test how the PM transfers to a less-symmetrical system based on an exhaustive study of its phonon dispersion curves by INS, using hexagonal-Zn1 xMgxS (x=0.33) as a case study. In parallel, its phonon-polariton dispersion will be studied by (forward) RS to complete an overview of the Zn1 xMgxS lattice dynamics, yet unexplored experimentally

Proposal : 7 – 01 – 598

Title : Percolation scenario for hexagonal semiconductor alloys : A test case by applying inelastic neutron scattering to wurtzite-$Zn_{0.67}Mg_{0.33}S$

Instrument : IN8 From 13/09/2023 to 19/09/2023 – Original beamtime allocation

IN8 From 25/03/2024 to 27/03/2024 – Follow-up

Instrument Responsible : Dr. Alexander Ivanov

Co-proposers: T. Alhaddad, A. Elmahjoubi, O. Pagès, A. Polian, A.V. Postnikov and M. N. Rao

Aim

Inelastic neutron scattering is used to study how the percolation scheme [1] worked out to explain the lattice dynamics of the high-symmetry cubic (zincblende-zb) $A_{1-x}B_xC$ semiconductor alloys transfers to a lower crystal symmetry, using the hexagonal-$Zn_{1-x}Mg_xS$ (wurtzite-w) alloy as a case study. Basically, within the percolation model (PM) the optic modes distinguish, beyond bond species, "same" (*homo*) from "alien" (*hetero*) environments of a given bond (1-bond→2-mode [1]), and thus "see" the local fluctuations in composition inherent to random alloying. This deviates from the historical modified-random-element-isodisplacement (MREI, [2]) model in which the O-modes are "blind" to such fluctuations, the like bonds of a given species vibrating at the same frequency at a given alloy composition (1-bond→1-mode), irrespectively of their local environment.

More generally, the w-$Zn_{1-x}Mg_xS$ lattice dynamics remains unexplored experimentally, either by inelastic light (Raman – RS) scattering or by inelastic neutron scattering (INS), so that the planned INS study of wurtzite $Zn_{1-x}Mg_xS$ is interesting *per se*.

The (Zn; Mg; S) combination is well suited for INS due to their small neutron absorption cross sections σ_{Xs} = (0.9; 0.1; 0.5) barn [3] and high coherent neutron scattering lengths b_{coh} = (5.2; 5.7; 2.8) fm [4].

Methods

- *Samples*

The INS experiment on $Zn_{1-x}Mg_xS$ is carried out on two large homogenous (checked by Raman mapping across the ingots) free-standing single crystals with wurtzite structure verified by powder X-ray diffraction, grown using the Bridgman method [5] at

- high alloying : $Zn_{0.67}Mg_{0.33}S$, half-cylinder 15×8 mm^2 in length×diameter
  1st experiment 13 – 19 sept. 2023
- low alloying: $Zn_{0.94}Mg_{0.06}S$, cylinder 6×8 mm^2
  2nd experiment/ follow up 25 – 27 march 2024

High quality of crystal structure is attested by sharp peaks in the powder X-ray diffractograms. The single crystals are oriented by conoscopy ($\overrightarrow{c^*}$ axis), X-ray diffraction and neutron diffraction *in situ* ($\overrightarrow{c^*}$ and $\overrightarrow{a^*}$ axis). The composition x is determined with accuracy up to 0.1% by the inductively coupled plasma method.

- *Experiment*

INS experiments are conducted at the thermal neutron three-axis spectrometer IN8 at the high flux reactor of the Institut Laue-Langevin. The 2D-focusing copper monochromator with reflection planes Cu-(200) and pyrolytic graphite (PG) analyser with reflection planes PG002 provide optimal spectral resolution of the O-modes using scattered neutron wave vector 2.662 $Å^{-1}$. Higher order contaminations in the monochromatic beams are practically entirely removed with a 10 cm thick oriented pyrolytic graphite filter. The INS spectra are measured at sample temperature of 12 K in the $\overrightarrow{c^*}/\overrightarrow{a^*}$ scattering plane at various phonon wave vectors across the BZ along $\overrightarrow{c^*}$ and $\overrightarrow{a^*}$. Both the acoustic and optic modes are probed for w-$Zn_{0.67}Mg_{0.33}S$ (**1st experiment 13 – 19 sept. 2023**), whereas only the non-polar O-modes, of main interest, for w-$Zn_{0.94}Mg_{0.06}S$ (**2nd experiment/ follow up 25 – 27 march 2024**). Experiment is guided by dynamical structure factor computations using the shell model [6], that helps to target special BZ in the periodic zone scheme (shifted from the first BZ by a reciprocal lattice vector $\vec{G}$) as the best compromises between maximal neutron scattering cross section and optimal symmetry (transverse or longitudinal) access.

- *Ab initio* calculations

Ab initio phonon dispersions of w-$Zn_{0.67}Mg_{0.33}S$ are calculated with the SIESTA code based on the density functional theory (DFT), using specifically the local density approximation (LDA), by the *finite displacement* technique. Two large (360-atoms) special quasirandom structures [7] are used, optimized to a random Zn↔Mg substitution with the help of the Alloy Theoretic Automated Toolkit (ATAT [8]). The supercells are elongated in a sequence of ten base-slices cut normal to [001] and [100] directions. Each slice is one primitive cell thick and has

lateral size of 3×3 primitive cells. Once the *finite displacement* calculation is performed for a supercell, different projections of the set of 3N (N: number of atoms) vibration eigenvectors are applied in order to reveal different trends – as explained in Sec. N.3 of Ref. [9]. In this work, combined projections onto $\vec{q}$ wavevectors and onto irreducible presentations of the wurtzite space group enable extraction of the "spectral functions", resolved in frequency and wavevector, to be directly confronted with the INS w-$Zn_{0.67}Mg_{0.33}S$ phonon dispersions.

Results

A dispersion of the PM-type dual O-modes of w-$Zn_{0.67}Mg_{0.33}S$ is searched for by INS across the BZ along the $\overrightarrow{c^*}$ and $\overrightarrow{a^*}$ high-symmetry reciprocal lattice directions. The additional w-$Zn_{0.94}Mg_{0.06}S$ alloy with minimal Mg content preserving the hexagonal structure is used as a "negative" PM-control, meaning that the PM-duo should not show up in this case (because alloying tends to zero). The discussion of the INS data is supported by *ab initio* phonon calculations (using the SIESTA code) done on large (up to 360-atom) disordered w-$Zn_{1-x}Mg_xS$ supercells at high (x=0.33) alloying. The *ab initio* insight is used as a "positive" PM-control – meaning that any presumed PM-duo seen by INS should replicate *ab initio* if intrinsic to random Zn↔Mg alloying (x=0.33).

In practice, the PM-test focuses on the non-polar $\{A_1(TO), E_1(TO), B_1^H, E_2^H\}$ O-modes, that hardly couple and thus preserve the natural diversity of the O-modes in a complex system like an alloy. The first three are probed in their dispersion along $\overrightarrow{c^*}$ and the fourth one along $\overrightarrow{a^*}$. The $E_1(TO)$, E_2^H, $A_1(TO)$ and B_1^H dispersions measured by INS at high alloying on w-$Zn_{0.67}Mg_{0.33}S$ are discussed in comparison with their counterparts calculated *ab initio* on large special quasirandom structures, used as "positive" PM-controls (as defined above), and in the light of additional dispersions measured by INS at low alloying on w-$Zn_{0.94}Mg_{0.06}S$, used as "negative" PM-controls. An example presented in the format of a triptych combining *(2×) experimental (x=0.06; 0.33) vs. (1×) ab initio insights (x=0.33)* is given for E_2^H in **Figure 1**. A distinct PM-type duo is evidenced for the Zn-S bond across the entire Brillouin zone, better resolved near the Brillouin boundary.

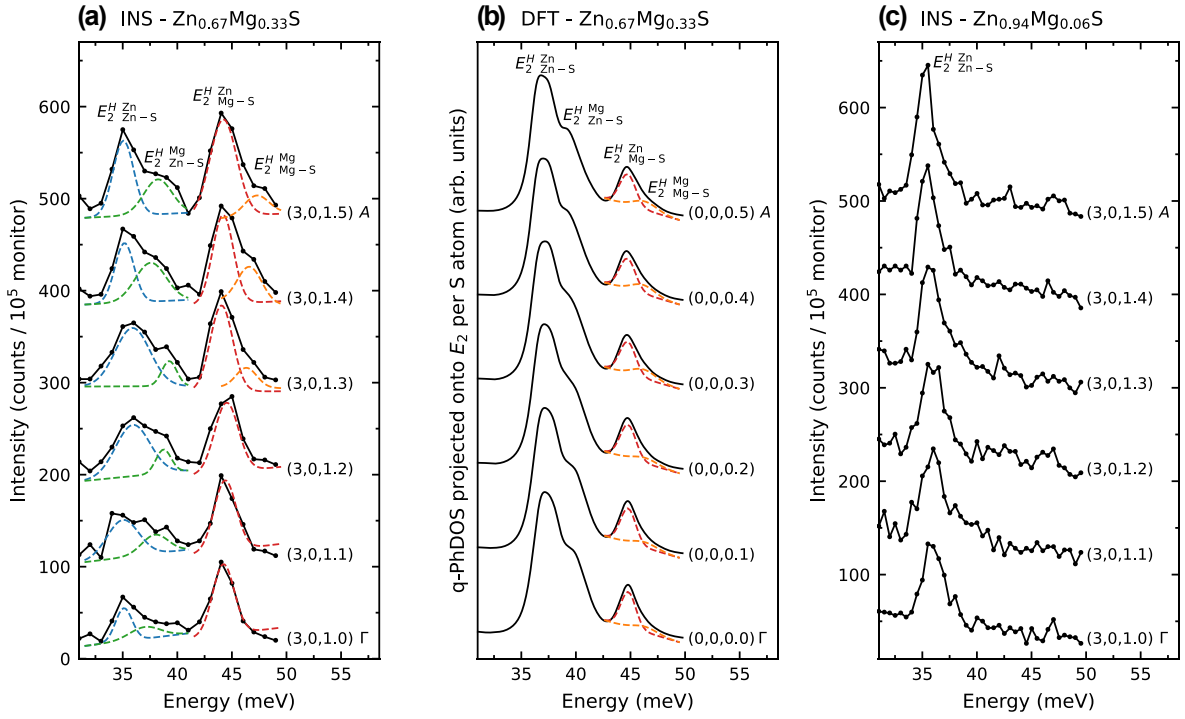

Figure 1 | E_2^H phonon dispersion of wurtzite (w) $Zn_{1-x}Mg_xS$. (a) E_2^H phonon dispersion of w-$Zn_{0.67}Mg_{0.33}S$ measured by INS along $\overrightarrow{c^*}$. The dual Zn-S and Mg-S signals (subscript) are deconvolved for clarity (colored dashed lines), distinguishing *homo* from *hetero* environments (superscript). **(b)** Corresponding E_2^H phonon dispersion per S atom calculated *ab initio* (SIESTA DFT) using the w-$Zn_{0.67}Mg_{0.33}S$ special quasirandom structure. **(c)** Corresponding E_2^H phonon dispersion of w-$Zn_{0.94}Mg_{0.06}S$ measured by INS.

Conclusion

The PM-test on hexagonal $Zn_{1-x}Mg_xS$ is positive for all tested $\{A_1(TO), E_1(TO), B_1^H, E_2^H\}$ O-modes: Similar PM-type duos are evidenced for Zn-S bond in all cases. This validates the PM as a reliable model of the optic modes of semiconductor alloys across cubic→hexagonal crystal symmetries.

Publication

A manuscript entitled

Lattice dynamics of hexagonal $Zn_{1-x}Mg_xS$

co-authored by

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is currently submitted for publication in an international journal.

The manuscript is referenced on ArXiv at

arXiv:2503.03381 **[cond-mat.mtrl-sci]**, https://doi.org/10.48550/arXiv.2503.03381

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On behalf of co-authors

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