Electronic and vibrational properties of electron-doped transition-metal nitride halides *R*N*X* (*R* = Zr and *X* =Br, I) from first principles

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Abstract:

Using density functional theory (DFT), we study transition-metal nitride halides *R*N*X* (*R* = Zr; *X* = Br, I). The metal nitride halides *R*N*X* form two different polymorphs (α and β) in their layered crystallized structures. The parent compounds are band insulators, that when electron-doped, become superconductors. We used DFT calculations to obtain the energy as a function of electron density. We will discuss the electronic band structure of *R*N*X* materials and the effects of electron doping on these materials in β-form.

Introduction:

Superconductivity is one of the most captivating quantum experiences that the natural world has created. It is the property of certain materials to conduct electricity below what is known as the critical temperature T_c with zero resistance. We are studying the superconductivity of the metal nitride halides *R*N*X* (*R*= Zr; *X*= Br, I), which are indirect bandgap semiconductors with a layered structure, by electron doping. These compounds are considered band insulators, so we are using these two-dimensional host crystals to intercalate with the alkali metal lithium to assist in modifying the physical attributes without altering the fundamental crystal structures at high temperatures. Transition metal nitride layers are considered promising superconductors, similar to CuO_2 for the purpose of doping by intercalation. Intercalation manipulates the aperture within the crystal structures, and a high level of doping is conceivable [1]. An example of these newly developed, layered-structure nitrides is ZrNCl, which we studied to gain insight into its superconductivity. Research had shown for ZrNCl that at a low-doping regime the superconducting critical temperature increases [1-3].

Methods:

We performed first-principles calculations using the Quantum-ESPRESSO software package [4]. Throughout our process, we generated experimental cell parameters using previous research [5] as well as converted the cell parameters for our electron-doped beta structures from hexagonal to rhombohedral cell. The different pseudopotentials were generated with a non-relativistic calculation and the exchange-correlation potential has been defined utilizing the PBE functional. The calculations were performed using a kinetic energy cutoff of 70 Ry, a Methfessel-Paxton smearing of 0.02 Ry, and an electronic momentum k-mesh of 12x12x12.

Results:

Our interest was in the halides and knowing what would happen if we switched chloride in previous research [2-3] with bromide and iodide that are being used in our research. We found that the α-form polymorph crystallizes in the orthorhombic space group *Pmmn* (#59). The β -form polymorph crystallizes in the rhombohedral space group *R*3*m* (#166).

We studied both semiconducting structures and compared their electronic structures using DFT. Both α-ZrNBr and α-ZrNI are semiconductors with parabolic bands between Γ - X and Γ - Y. α-ZrNBr has a direct band gap of 1.810 eV (shown in Fig. 1) and α-ZrNI has a direct band gap of 1.247 eV (shown in Fig. 2) at the Γ point.

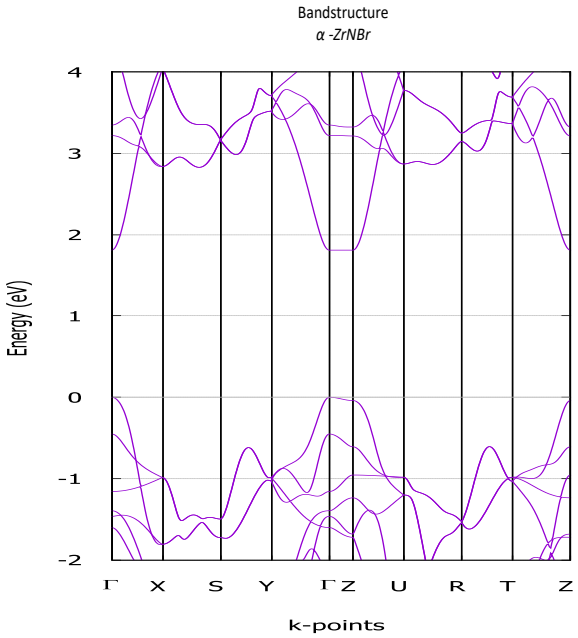

Figure 1: Electronic band structure of α-ZrNBr.

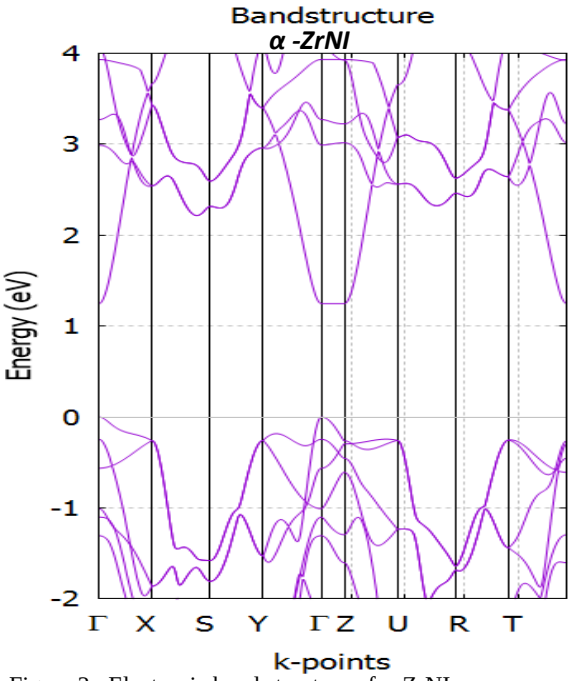

Figure 2: Electronic band structure of α-ZrNI.

ZrNBr exists in the β-phase similar to β-ZrNCl in previous research. Figure 3 shows that β-ZrNBr is a semiconductor with a single parabolic conduction band centered around the K-point. It has a band gap of 1.441 eV. As it is doped, the Fermi level shifts upward.

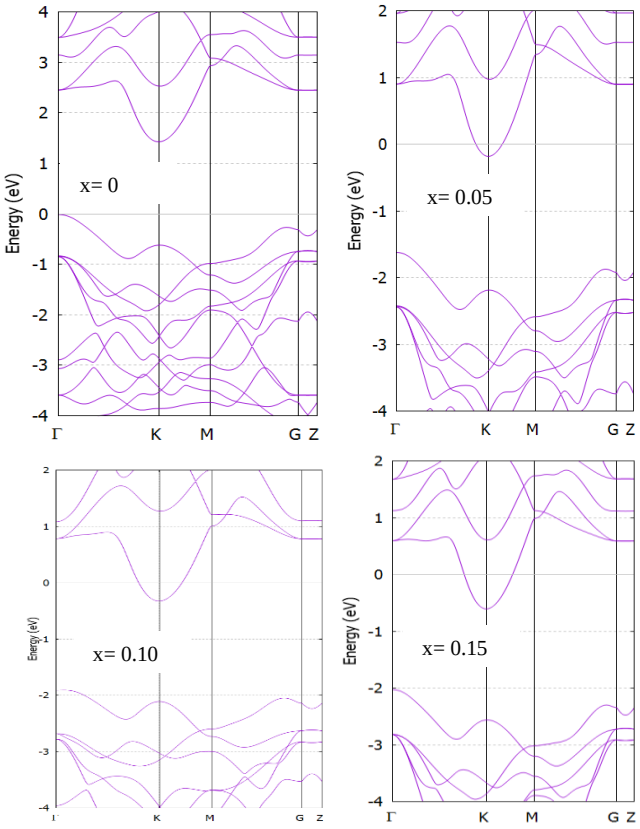

Figure 3: Electronic band structures of β-ZrNBr with and without electron doping. The Fermi level is set to 0 eV, with x representing the amount of electron doping per formula unit in Li_xZrNBr.

Understanding the electronic structure of these materials will help us further explore how superconductivity can be controlled.

Future Work:

For future work, we would like to calculate the vibrational properties better known as the phonons. We also would like to calculate the superconducting temperature.

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