**Unveiling excitonic insulator signatures in Ta2NiSe5 through structural**

**and orbital probes**

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The concept of an excitonic insulator (EI) was theoretically proposed nearly 60 years ago. It was predicted that poorly screened coulomb interaction between conduction band electrons and valence band holes can lead to the formation of charge-neutral quasi-particles (excitons), which have the potential to condense in an unconventional insulating ground state as EI [1, 2]. Despite decades of investigations, conclusive experimental evidence of its existence remains elusive [3, 4]. Ta2NiSe5 is one of the few promising candidates for an EI due to its zero-gap semiconducting high-temperature phase. It undergoes a structural phase transition from an orthorhombic to a monoclinic phase, accompanied by a semiconductor- or semimetal-to-insulator transition at *T*c which is assumed to be driven by an EI origin [5–7].

Given the dome-like evolution expected for an excitonic insulator around *E*G = 0, we tuned the electronic band gap of the Ta2NiSe5 by cobalt and sulfur substitution on the Ni and Se sites, respectively. Co substitution increases the negative band gap, driving the system into the semimetal region, while S substitution shifts the system toward the semiconductor region [6, 8].

To thoroughly examine the existence of an EI state in these systems, we investigated the three compounds, Ta2NiSe5, Ta2Ni0.93Co0.07Se5 and Ta2NiS5, using high-resolution single-crystal X-ray diffraction (SXRD) and near-edge X-ray absorption fine structure (NEXAFS). Our SXRD data reveal that not only Ta2NiSe5 but also Ta2Ni0.93Co0.07Se5 undergoes a second order structural phase transition from orthorhombic (*Cmcm*) to monoclinic (*C*2/*c*) symmetry, where mirror breaking enables hybridization of the Ta, Ni and Se atom orbitals, and the shortening of the bond lengths enhances orbitals interaction. In comparison, no evidence of a structural change is found in Ta2NiS5 down to 2 K. These results are fully consistent with the NEXAFS data, where observed changes in the orbital characters indicate the formation of an EI state and even permit the identification of the orbitals involved in the process. This effect is most pronounced in Ta2NiSe5, significantly reduced in Ta2Ni0.93Co0.07Se5, and nearly absent in Ta2NiS5.

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