Assigning the origin of unusually stable cation vacancies in II-VI semiconducting systems

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II-VI semiconductors are some of the earliest-studied class of semiconductors, historically exhibiting great potential in optoelectronics applications such as photovoltaics, LEDs and luminescence-based devices, alongside relatively benign synthesis routes. Despite this, theoretically-predicted properties of these compounds have been inconsistent with experimental results, often underestimating the effect of vital processes such as non-radiative carrier recombination [1], or dopant concentrations. In attempting to understand the origins of these oversights in the context of point-defects, the recently developed ShakeNBreak [2] structure-searching algorithm has unearthed the necessity of a symmetry-breaking approach for accurately scoping the potential energy landscape of the defected material. Thus, many previous theoretical predictions have been found to actually detail the performance of metastable structures [3], leading to a poor and unphysical representation of stable defect types and charge states.

This study focuses on identifying the ground-state structures and their properties in the specific case of cation vacancies in binary II-VI semiconductors. These defects are often overlooked due to the fixed-valency of the cations, but recent studies in CdTe [4], Sb_2Se_3 [5] and ZnS have shown a wider range of stable charge states within these materials that contradict previously reported papers [6]. Furthermore, the stabilisation of such charge states stems from an array of interesting mechanisms, such as “defect-migration”, and anionic valence-alternation. As a result, this study reports on the trends within these mechanisms and materials, in the hope that they can explain defect stability in a wider range of materials and applications.

This is achieved through a first-principles assessment of cation vacancies in various binary II-VI compounds, using DFT with the hybrid-functional HSE [7] (with varying HF-mixing and SOC consideration). Using the ShakeNBreak [2] methodology, the structures and associated potential energy surfaces for these materials are identified. Following this, the *DOPED* defect analysis package [8] is used to identify the formation energies and spin-dependent charge localisation in each system, before relating them to experimental data. We hope that this work can provide a deep insight into the methodology required for effective theoretical estimations of such materials, to enable better material design for the future.

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