Photoemission study of the thermoelectric group IV-VI van der Waals crystals (GeS, SnS, and SnSe)

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Semiconducting group IV-VI van der Waals crystals (MX, where M = Ge, Sn, and X = S, Se) are receiving increasing attention as environmentally-friendly thermoelectric materials. Among them, SnSe is considered the most promising as it exhibits a remarkably high thermoelectric figure of merit (ZT), initially attributed to its low lattice thermal conductivity [1]. However, it has been shown that the electronic band structure plays an equally important role in thermoelectric performance [2,3]. A certain band shape, described as a "pudding mold" and characteristic for all MXs, has been predicted to significantly improve ZT by combining good electrical conductivity with high Seebeck coefficient [4]. We explore this subtle feature experimentally for GeS, SnS, and SnSe by means of angle-resolved photoemission spectroscopy. The technique also allowed us to determine the effective mass and Fermi level position of as-grown undoped crystals. Our findings are supported by *ab initio* calculations of the electronic band structure. The results greatly contribute to the general understanding of the valence band dispersion of MXs and reinforce their potential as high-performance thermoelectric materials, additionally giving prospect for designing systems consisting of van der Waals heterostructures.

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