

Mechanism of electron-rich multicenter bonding in elemental crystals under pressure

Hussien H. Osman

University of Valencia, Spain

The unconventional bonding in the crystalline phases of phase change materials (PCMs) has been discussed in the literature using different chemical bonding models.[1-8] One of those models proposes that PCMs feature electron-rich multicenter (ERM) bonds related to materials with a pre-ERM bonding scenario characterized by a combination of a primary covalent σ -bond and a secondary bond in which the lone electron pairs (LEPs) are involved.[2,4-8] Since the pre-ERM bonding scenario occurs in group-V (As, Sb, Bi) and -VI (Se, Te) elements,[9] we show, by means of quantum-mechanical calculations, that these elements develop ERM bonds at high pressure as they approach sixfold coordination. Interestingly, polonium, in both its α - and β - phases, is the only element that shows ERM bonds at room pressure. We also show that the ERM bond formation mechanism, which can show up to three stages, depends on the type of LEP present in secondary bonds. This work provides a comprehensive understanding of the ERM bond formation that is key to improving the performance of advanced materials, such as PCMs, topological insulators, and highly efficient thermoelectrics of the IV-VI and V2-VI3 families.

- [1] P. B. Littlewood, *Crit. Rev. Solid State Mater. Sci.* 1983, 11, 3, 229.
- [2] A.V. Kolobov, P. Fons, J. Tominaga, and S.R. Ovshinsky, *Phys. Rev. B* 2013, 87, 165206.
- [3] M. Wuttig, V. L. Deringer, X. Gonze, C. Bichara, J.-Y. Raty, *Adv. Mater.* 2018, 30, 51, 1803777.
- [4] T. H. Lee, S. R. Elliott, *Adv. Mater.* 2020, 32, 28, 2000340.
- [5] T. H. Lee, S. R. Elliott, *Phys. Status Solidi RRL* 2021, 15, 2000516.
- [6] J. Hempelmann, et. al., *Adv. Mater.* 2021, 33, 37, 2100163.
- [7] J. Hempelmann, et. al., *Angew. Chem., Int. Ed.* 2022, 61, 17, e202115778.
- [8] T. H. Lee, S. R. Elliott, *Nat. Commun.* 2022, 13, 1 1458.
- [9] M. Kastner, *Phys. Rev. Lett.* 1972, 28 355.