# Electron-Rich Multicenter Bonding in Elemental Crystals Under Pressure: Basic concepts and Bonding Mechanism

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## Abstract

Comprehensive understanding of the chemical bonding nature in materials plays a crucial role to explain their structure and physico-chemical properties as well as to envisage their applications. An unconventional electron-rich multicenter (EMR) bond has been recently proposed to be present in crystalline phases of binary and ternary compounds related to IV-VI and $V_2$-$VI_3$ families of phase change materials, topological insulators, and highly-efficient thermoelectric materials. While crystalline phases with sixfold atomic coordination, such as the cubic rocksalt phase, feature an EMR bond (also noted in the literature as hypervalent, 3c-4e, resonant, or metavalent bond), crystalline or amorphous phases with smaller atomic coordination are Jones-Peierls-distorted structures of the cubic rocksalt phase characterized by a combination of ppσ-covalent plus secondary bonds in which the lone electron pairs (LEPs) are involved.

Here we show, by means of theoretical quantum bond descriptors, that group-15 (As, Sb, Bi) and -16 (Se, Te) elements undergo a gradual bonding change and develop ERM bonds at high pressures once they approach the sixfold atomic coordination. The only exception is Po, which is the only element whose crystalline α and β structures exhibit ERM bonds at room pressure. We prove that structures with mainly ppσ-covalent bonds are characterized by the presence of soft optical phonons that show the intrinsic instability of these bonds under compression and that the gradual pressure-induced bonding change shows a universal mechanism proceeding through several stages depending on the orbital character of the LEPs involved in secondary bonds as shown in **Figure 1**. These findings provide a comprehensive framework to understand the formation of ERM bond in solid elemental and complex materials and open the door for a better understanding of the chemical bonding mechanisms in advanced materials for improving their performance.

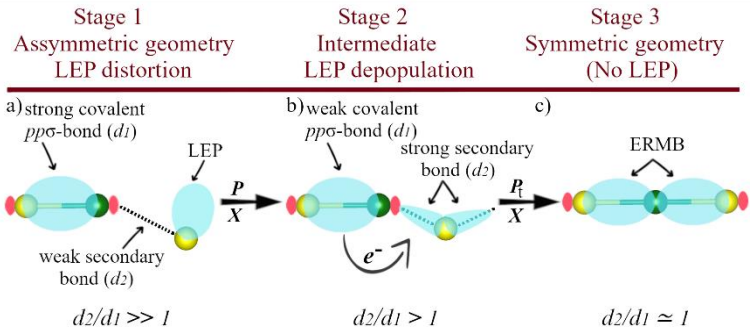



**Fig. 1.** Graphical representation of the mechanism of ERM bond formation in a 3c-4e model system under the effect of hydrostatic pressure (*P*) or change of chemical composition (*X*).

**Keywords**: Multicenter, hypervalent, 3c-4e, resonant, metavalent, chemical bond, lone pair electrons, high pressure