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The Myth of "Metavalency" in Phase-Change Materials

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Phase-change memory materials (PCMs) have unusual properties and important applications, and recent efforts to find improved materials have focused on their bonding mechanisms. "Metavalent bonding" or "metavalency," intermediate between "metallic" and "covalent" bonding and comprising single-electron bonds, has been proposed as a fundamentally new mechanism that is relevant both here and for halide perovskite materials. However, it is shown that PCMs, which violate the octet rule, have two types of covalent bond: two-center, two-electron (2c-2e) bonds, and electron-rich, multicenter bonds (3c-4e bonds, hyperbonds) involving lone-pair electrons. The latter have bond orders less than one and are examples of the century-old concept of "partial" bonds.

1. Introduction

Phase-change memory materials (PCMs), such as GeTe, Sb_2Te_3, and their solid mixtures, exhibit extremely rapid and reversible crystallization of amorphous regions in thin polycrystalline layers. The phase changes are usually triggered by voltage or laser pulses of appropriate intensity and duration, and the nature of the metastable states can be determined by measuring the pronounced differences in electrical resistivity or optical reflectivity between the two phases. Non-volatile binary or analog information can therefore be stored by means of the atomic arrangement, and essential attributes of PCMs including rapid crystallization, long-term stability, and property contrast of the two phases.

Investigations over several decades have shown that materials with the most favorable properties are often narrow-gap semiconductors comprising a small number of heavy main-group elements, generally with more valence electrons than expected from the octet rule, which requires that atoms of main-group elements have four pair-bonds. Sb and Te are almost always present, often with compositions near the tie-line $(GeTe)_{1-x}(Sb_2Te_3)_x$ (GST)[1] or in alloys near the eutectic composition $Sb_{0.7}Te_{0.3}$, sometimes with small amounts of other elements.[2] The ongoing search for correlations between the properties of candidate materials is essential for the identification of PCMs with improved capabilities. Experimental quantities studied include the dielectric constant,[3] and the results of recent electronic structure calculations were presented in terms of the number of electrons shared or transferred between atoms[4] (**Figure 1**).

These "maps" have been used to assign particular bonding "mechanisms" to different families of PCMs, although a sharp distinction is not always possible. Families with favorable properties were identified initially as showing "resonant bonding" in the crystalline state,[3] but "resonance" is a controversial term in quantum mechanics,[5] and its use here has given way recently to "metavalent bonding" (refs. [4,6,7] and references therein). The underlying assumption is that the unexpected differences between the properties of crystalline and amorphous PCMs, including bond-breaking mechanisms and vibrational frequency distributions, must be due to a bonding mechanism in the former that is *fundamentally different* from more familiar forms ("covalent," "metallic," and "ionic") and therefore warrants a new name. These bonds are assumed to involve a single p-electron shared between adjacent atoms[7] and arise from the competition between electron localization—assumed to be present in "ionic" and "covalent" bonding—and delocalization expected in "metallic" bonding.[7] The materials are referred to as "incipient metals,"[8] and the approach has been extended recently to halide perovskites.[9] The focus on the experimentally observable charge density (Figure 1) follows the quantum theory of atoms in molecules of Bader.[10]

Based on our recent independent works (refs. [11–14] and references therein), work by others,[15] and a thorough study of the earlier chemical literature,[16] we show here that the bonding in PCMs can be understood without invoking an "unconventional, new bonding mechanism."[6] "Partial" bonds with fewer than two electrons, in particular single-electron bonds, have been used for at least 100 years to explain the chemical behavior of molecules that do not satisfy the octet rule.

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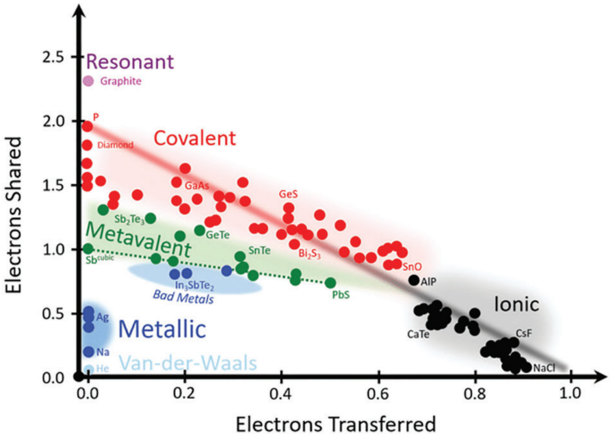

Figure 1. The number of electrons shared between adjacent atoms for a range of crystalline materials plotted against electron transfer (renormalized by the formal oxidation state). The bonding mechanisms identified in ref. [4] are also shown. Reproduced with permission.[4] Copyright 2021, The Authors, published by Wiley-VCH.

2. The Chemical Bond

2.1. General

The history of the chemical "bond" from its inception in 1866 is surveyed in ref. [5] and two generally accepted classes are "covalent" (or "polar/covalent") and "ionic" bonds.[17,18] Ionic bonds are familiar in the solid state context, where electrostatic interactions between, for example, the Na^+ and Cl^- ions in rock salt stabilize the structure by a large Madelung energy. On the other hand, a microscopic understanding of covalent bonding was not possible before the advent of quantum mechanics, and the prototype calculations for H_2 using the molecular-orbital (MO)[19] and valence-bond (VB)[20] approximations followed very soon after publication of the Schrödinger equation (ref. [21] and references therein).

Heitler and London[20] showed that interference of the electronic wave functions of the component atoms is essential to explain the bonding in H_2, and different choices of phase allow one to describe its bonding and antibonding states. This is not possible using classical, electrostatic models, such as a superposition of atomic densities, since the wave function Ψ determines the electron density $\rho = \Psi^2$ unambiguously, but the reverse is not true.[22] If the phases are unknown, the density alone provides neither information about the symmetry of the molecule nor a physically consistent picture of the mechanism of bond formation. A similar problem exists in crystallography with intensities and structure factors.

In the MO approach to molecular structure, electrons are viewed as moving under the influence of all atomic nuclei. The orbitals are usually expanded in terms of atomic-centered functions, occupied according to Fermi statistics, and designated as bonding (constructive, in-phase combination), antibonding (destructive, out-of-phase combination), and non-bonding (no overlap). If necessary, the delocalized orbitals of MO calculations can be converted to a localized description of the electronic structure by unitary transformations.[23] The quantum mechanical view of covalency does not require electron pairing; occupancy of a bonding orbital by a single electron, as in H_2^+, also leads to a "covalent" bond. In fact, the dissociation energies of the one-electron bonds in all alkali dimer cations Li_2^+–Cs_2^+ are larger than in the corresponding neutral dimers.[24]

Ionic bonds, for example in NaCl, result from the lowering of the *potential* energy as charges of opposite sign approach each other. This is a classical, electrostatic interaction between an electron and a hole with spatially separated one-center wave functions (atomic orbitals). The balance between kinetic and potential energy in covalent bonding is more subtle, however, and it was many years before the driving force for bond formation was identified as the lowering of the *kinetic* energy due to the *interatomic* delocalization (expansion) of the molecular wave function as atoms come closer.[25,26] This was first demonstrated by Ruedenberg[27] for H_2^+ and H_2, and he and his collaborators studied diatomic molecules up to F_2 over many years (ref. [28] and references therein). Delocalization of the wave function across neighboring atoms is also essential to describe bonding in metals, and the similarity to the covalent picture has led to calls to abandon use of the term "metallic bonding" altogether (ref. [16] and references therein). Binding in metals can be viewed simply as covalent bonding among many atoms with few electrons.

Electron pairing is a consequence of the Pauli principle and has obvious consequences for the electronic structure of molecules. Nevertheless, the Lewis picture[29] of bonding, with an electron pair localized between two atoms (the two-center, two-electron (2c-2e) bond) must be modified. The triplet ground state of the O_2 molecule shows that the occupancy of an orbital by a pair of electrons with opposite spins is not a general rule, NO has an odd number of electrons, and Lewis did not consider multicenter bonds.

If there are more electrons than those needed to satisfy the octet rule, the molecules are often designated as "electron-rich" or "hypervalent,"[30] terms often used "interchangeably".[31] Binding here is usually explained by the three-center, four-electron (3c-4e) picture of Pimentel[32] and Hach and Rundle[33] with the orbital occupancies as shown in **Figure 2**. It is sometimes overlooked[7] that the presence of formally non-bonding electron pairs ("lone pairs") means that the bond order between adjacent atoms in this 3c-4e bond is 0.5, and the bond can be viewed as a pair of collinear 2c-1e bonds.[34] Coulson noted that "no essentially new type of bonding need be postulated" in a σ-bonded, electron-rich, three-center molecule like F–Xe–F.[35]

"Multicenter bonding is a natural extension of covalent electron-pair bonding to electron-deficient or electron-rich systems,"[31] and the former can be understood as 3c-2e bonds,[36] again with "half-bonds" between atoms (Figure 2). Partial bonds ("one-electron covalencies"[37]) have a long history,[16] and the borane (B_2H_6) molecule shows that they can occur together with 2c-2e bonds. Sugden noted over 90 years ago that molecules containing atoms from groups 15–18 of the periodic table, such as PCl_5, could be viewed as covalent compounds that do not violate the octet rule, provided that some of the bonds "are composed of one shared electron."[38] The relative strengths of one-electron and pair bonds can best be shown when they join the same type of atom in the same molecule, for example, PCl_5.[38]

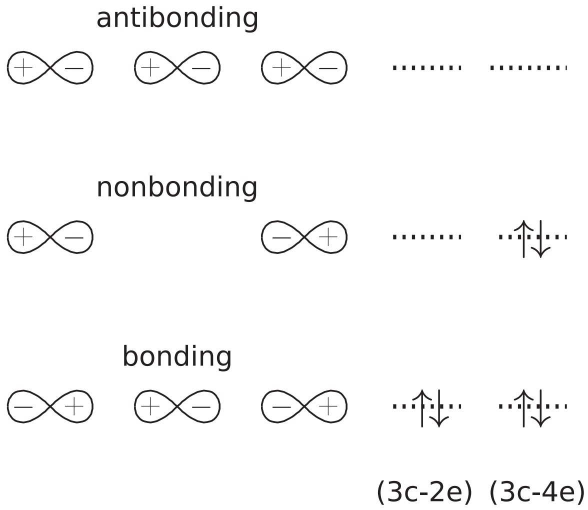

Figure 2. Low-lying molecular orbitals and their occupancies in 3c-2e and 3c-4e "bonds" in a linear system with p-electrons. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0).[16] Copyright 2022, The Author, published by IOP Publishing.

2.2. Bonding in Phase-Change Materials

Few of the many compounds investigated during PCM development were found to have favorable properties or be commercially viable. The "secret" (or "key") to finding the "ideal" materials along the GST tie-line $(\mathrm{GeTe})_{1-x}(\mathrm{Sb_2Te_3})_x$ lay in the existence of metastable, distorted rock salt structures containing cationic vacancies,[1] the fraction of which varies approximately as $x/(1+2x)$.[39] The average valence configuration per site (including vacancies) is close to five valence electrons [4.71 in GST-147 ($x = 2/3$), 4.75 in GST-124 ($x = 1/2$), 4.80 in GST-225 ($x = 1/3$), 4.91 in GST-8,2,11 ($x = 1/9$)], with three p-electrons in each case. Configurations with three singly-occupied, orthogonal p_x, p_y, and p_z orbitals are often associated with cubic structures.[40] In fact, amorphous GST films crystallize to an NaCl cubic-like phase if $x \geqslant 1/7$ or to a closely related rhombohedral phase for GeTe-rich samples ($x \leqslant 1/9$).[39]

Tellurium provides at least half of the atoms in GST compounds, and tellurides dominate the "metavalent" region of Figure 1. Te has the valence configuration $5s^2 5p^4$, so that the presence of lone pairs is inevitable in materials where the Te concentration dominates. The amorphous (refs. [12, 41] and references therein) and crystalline[11] forms of the prototype PCM $\mathrm{Ge_2Sb_2Te_5}$ (GST-225, $x = 1/3$) show linear structural units with more than two collinear bonds, with a higher concentration in the crystalline phase.[12] The pronounced peaks near 90° in the bond-angle distributions of Te–Sb–Te and Te–Ge–Te structural fragments in amorphous GST-225[41] are consistent with the tendency to octahedral coordination, and the presence of vacancies complies with the presence in vacancy-free GST-224 of occupied, *antibonding* levels for Ge–Te and Sb–Te interactions.[42,43] An orbital analysis of the crystalline structures of five GST-compounds [14] supports the picture of electron-rich multicenter bonding and explains the unusually small "van der Waals" gap in layered PCM compounds.[14] It is well established that 3c-4e bonding, hyperbonding, hyperconjugation, and secondary bonding interactions play much more important roles in molecules and materials containing Te than in those containing S or Se.[44]

Te compounds have historically dominated the PCM field, and it is natural to ask why other chalcogens, particularly S and Se, are less prevalent. The electronegativity and the radial moments of the atomic orbitals in Te are very similar to those in Ge and Sb, but the corresponding values in S and Se show a distinct mismatch.[13] The valence orbitals in Se are more compact than those in Te due to the presence of occupied, high-lying 3d-electrons ("d-block contraction").[13] Ge/Sb/Se systems, for example, will generally have weaker bonds and less tendency to crystallize than Ge/Sb/Te compounds. It should be noted, however, that there is growing interest in sulfides and selenides for photonics applications. One example close to GST-225 is a study of the alloys $\mathrm{Ge_2Sb_2Se}_x\mathrm{Te}_{5-x}$, where the compound $\mathrm{Ge_2Sb_2Se_4Te_1}$ showed high broadband transparency, large optical contrast, and improved glass-forming ability over GST.[45] Phase-change memory materials, however, must crystallize extremely rapidly and are usually very poor glass formers, and the speed of crystallization of GSST materials is presently unknown. PCMs based on $\mathrm{Sb_2S_3}$ and $\mathrm{Sb_2Se_3}$, rather than $\mathrm{Sb_2Te_3}$, are suitable materials for photonic integrated circuits.[46]

The special status of Te is supported by recent simulations of S, Se, Te, and binary and ternary chalcogenides, which showed significant concentrations of linear 3c-4e bonds in tellurides, but negligible amounts in all crystalline and glassy models of sulfides and selenides.[12] Orbital analyses of crystalline GST-124 ($x = 1/2$)[42] and amorphous GST-225 ($x = 1/3$)[12] show that the highest occupied states in the valence band have an *antibonding* character with contributions from cationic lone-pair s-electrons. The existence of valence electrons with an s-antibonding character near the Fermi energy of group 15 elements and 14–16 compounds was noted many years ago.[40] The gap between the valence and conduction bands is smaller in tellurides than in sulfides and selenides, and a parallel to crystalline Bi, with overlapping valence and conduction bands and semimetallic properties, is evident.

A change in the bonding mechanism on crystallization of amorphous GST-225 has also been made responsible for differences in the vibrational properties, in particular that hardening of the low-energy acoustic phonons on crystallization is accompanied by a "unique" softening of the high-energy optical phonons.[47] We note, however, that disordering a crystal structure leads quite generally to mixing of phonon modes and a broadening of the vibrational density of states, to lower frequencies at the low-frequency edge and to higher frequencies at the high-frequency edge.[48] Phonon modes in crystalline GST-225 are naturally less localized than in the amorphous state.[49]

A recent study of group 15 elements and 14–16 crystalline compounds[50] adopts the language of "metavalent" bonding, while noting that its origin and distinction from other bonding forms are unclear. The authors write that the rock salt structures are "clearly electron-deficient and violate the $8-N$ (octet) rule," but conclude that "the bond-breaking mechanisms have their origin in multicenter bonding." They identify the metallic bonding and structural instability in the simple cubic forms of group 15 elements as "the parent metallic state of metavalently bonded materials," but overlook the work of H. Jones,[51] who applied the nearly-free-electron model of Peierls[52] to the element Bi ($6s^2 6p^3$) nearly 90 years ago. He showed that the simple-cubic structure is unstable against distortion to an A7 (rhombohedral) structure, the valence and conduction bands overlap, and the electron and hole pockets on the Fermi surface are consistent with the high diamagnetism and the low (semimetallic) conductivity of crystalline Bi. The mechanism of H. Jones[51] leads to precisely the structures with weakly broken symmetry and small bandgaps that are identified in ref. [50] as essential for "metavalent" bonding.

The dramatic changes from the properties of simple-cubic, *metallic* liquid Bi and other group 15 elements can, however, be understood without invoking any change in the bonding mechanism; crucial are the five valence electrons in the atom and a stable structure with two atoms per unit cell. For Ge, Sb, and Te, the electronegativities and the atomic valence orbitals, as measured by their radial moments, are very similar, and the same arguments applied to GST compounds with average valence near 5 explain their rhombohedral structures.[13] The formation of this structure is favored by the stronger bonds that result from the large overlap between the orbitals of neighboring atoms (ref. [13] and references therein).

A recent review of "metavalent" bonding in PCMs[7] criticizes descriptions of bonding based on the "fictitious" wave function Ψ and follows Bader[10] in focusing on the experimentally accessible ("physical") electron density ρ. The 3c-4e description of bonds in PCMs is dismissed as "misleading." Both criticisms are misplaced. The construction of molecular orbitals from experimental data is a reality,[53] not a fiction, and Ψ provides information not available from ρ that is essential to identify bonding mechanisms.[25] In the context of electron-rich systems, for example, the density provides no information about antibonding interactions of lone pair electrons with neighboring atoms, although they occur in all such systems. Furthermore, it is stated that multicenter (3c-4e) bonds in a cubic material like GeTe would require the involvement of 12 electrons, although partial bonds and fewer bonding electrons are guaranteed in such an electron-rich material. This was confirmed in ref. [14] where multicenter bonding in GeTe was quantified numerically.

3. Conclusion

The generation of a materials database has been essential to the development of PCMs and led ultimately to the discovery of the "ideal" materials, namely Ge/Sb/Te compounds.[1] The continuation and expansion of such investigations is essential to ensure the development of PCMs with improved properties, but recent years have seen significant focus on the mechanism of bonding in the crystalline state. The most recent proposal, "metavalent" bonding (refs. [4, 6, 7] and references therein) involves "electron-deficient" bonds[7,50] with single p-electrons (bond order 0.5) and is claimed to be distinct from covalent and metallic bonding. The supporting analysis was based on electron density distributions and charges shared and transferred between adjacent atoms (Figure 1),[4] without using the phase of the wave function.

In our view, identification of bonding *mechanisms* requires an analysis of the electronic wave function or the orbitals in density functional calculations. The electron density alone is insufficient, and the "metavalent" restriction to p-valence electrons is unjustified. Furthermore, the existence of "half-bonds" or "partial bonds" is an established feature of both 3c-4e bonds in "electron-rich" molecules and 3c-2e bonds in "electron-deficient" molecules. Our simulations have shown that linear structures involving 3c-4e bonds dominate in the rock salt structures of the crystalline phases of Ge/Sb/Te PCM, but are also present in the amorphous phases. We identify these as "covalent" bonds—expressed by either constructive orbital interference or being driven by kinetic energy lowering—as in metals, although with a larger electron count. It is therefore unnecessary and misleading to postulate a new bonding mechanism in PCMs and similar materials, such as halide perovskites.

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Conflict of Interest

The authors declare no conflict of interest.

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