Incipient Metals: Functional Materials with a Unique Bonding Mechanism

Matthias Wuttig, Volker L. Deringer, Xavier Gonze, Christophe Bichara, and Jean-Yves Raty*

While solid-state materials are commonly classified as covalent, ionic, or metallic, there are cases that defy these iconic bonding mechanisms. Phase-change materials (PCMs) for data storage are a prominent example: they have been claimed to show "resonant bonding," but a clear definition of this mechanism has been lacking. Here, it is shown that these solids are fundamentally different from resonant bonding in the π-orbital systems of benzene and graphene, based on first-principles data for vibrational, optical, and polarizability properties. It is shown that PCMs and related materials exhibit a unique mechanism between covalent and metallic bonding. It is suggested that these materials be called "incipient metals," and their bonding nature "metavalent". Data for a diverse set of 58 materials show that metavalent bonding is not just a superposition of covalent and metallic cases, but instead gives rise to a unique and anomalous set of physical properties. This allows the derivation of a characteristic fingerprint of metavalent bonding, composed of five individual components and firmly rooted in physical properties. These findings are expected to accelerate the discovery and design of functional materials with attractive properties and applications, including nonvolatile memories, thermoelectrics, photonics, and quantum materials.

Chemical bonding is not directly linked to quantum-mechanical observables and has been the topic of heated debates.[4] No less, understanding bonding is a key requirement for the discovery and design of new materials. Over the recent years, predictive bonding models have enabled the rational design of magnetic intermetallics,[5] supramolecular assemblies,[6] or novel thermoelectrics.[7] Today, quantum-mechanically and bond-theoretically driven high-throughput searches can point out target materials and compositions that had hitherto not been thought of.[8–10]

Materials scientists have recently rediscovered strong interest in a mechanism called "resonant bonding" in inorganic solids,[11–13] which has been linked to a portfolio of useful properties[14–17] but only described in empirical terms so far. The terminology itself goes back almost a century: Pauling's early work in the 1930s[18] proposed "resonant" bonding in the benzene molecule using a valence-bond framework. This concept is still part of every organic-chemistry textbook. The idea was later transferred to solids and suggested as an inherent property of several IV–VI semiconductors, based on experimentally observable quantities to which we will return

The structures and properties of materials are controlled by diverse interatomic interactions. Textbooks define the prototypical cases of covalent, ionic, and metallic bonding, but reality most often lies in between such idealized descriptions.[1–3]

Prof. M. Wuttig
Institute of Physics IA
RWTH Aachen University
52074 Aachen, Germany
E-mail: wuttig@physik.rwth-aachen.de

Prof. M. Wuttig
Peter Grünberg Institute (PGI 10)
Forschungszentrum Jülich
52428 Jülich, Germany

Dr. V. L. Deringer
Department of Engineering
University of Cambridge
Cambridge CB2 1PZ, UK

Prof. X. Gonze
Institute of Condensed Matter and Nanosciences
Université Catholique de Louvain
B1348 Louvain-la-Neuve, Belgium

Dr. C. Bichara
Centre Interdisciplinaire de Nanoscience de Marseille
CNRS and Aix-Marseille University
Campus de Luminy
Marseille, F 13288 Cedex 09, France

Dr. J.-Y. Raty
CESAM & Physics of Solids
Interfaces and Nanostructures
B5, Université de Liège
B4000 Sart-Tilman, Belgium

Dr. J.-Y. Raty
UGA
CEA-LETI
MINATEC campus
17 rue des Martyrs, F 38054 Grenoble Cedex 9, France

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201803777.

The copyright line for this article was changed on 2 November 2018 after original online publication.

DOI: 10.1002/adma.201803777

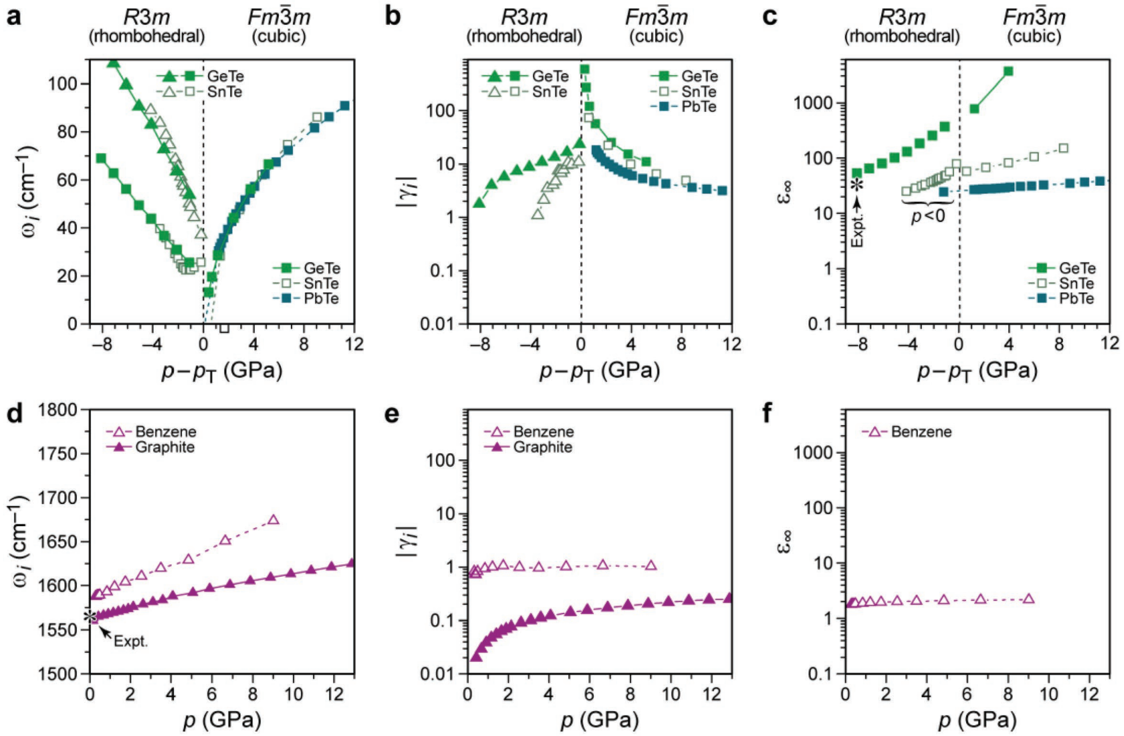

Figure 1. Physical properties of different materials thus far called "resonantly bonded," as obtained from first principles. a) Phonon frequencies, ω_i, for transverse optical modes in GeTe, SnTe, and PbTe as a function of pressure. Since GeTe and SnTe transform from a rhombohedral to a cubic structure, the respective transition pressure is set as reference ($p_T = 8.1$ GPa for GeTe, 0.7 GPa for SnTe). In contrast, PbTe takes an undistorted cubic structure at ambient conditions. For SnTe and PbTe, we include data at negative pressure p where needed, to obtain a more complete view of the behavior in the critical region. b) Absolute Grüneisen parameters, $|\gamma_i|$, for transverse optical modes, as an indicator for an anharmonic lattice instability. c) Optical dielectric constants, ε_∞, as an indicator for the electronic susceptibility. d–f) Same for the textbook examples of Pauling-like resonant bonding in molecules (benzene) and solids (graphene), respectively. No anharmonic behavior and no unusually high values of ε_∞ are observed. Hence, these materials are similar to common covalently bonded systems both in vibrational and optical terms. Where available, experimental data are included to ascertain the suitability of the computational method (asterisks); these data are taken from ref. [13] (c) and ref. [22] (d), respectively. The remarkable differences between the upper and lower panels suggest that the bonding nature in both materials classes must be fundamentally different, and that therefore the use of the term "resonant bonding" in PCMs needs to be abandoned.

below.[11,13] In parallel, a similar term is used for "resonating-valence-bond" materials such as high-temperature superconductors.[19] Clearly, the concept of resonance is invoked for very different material classes. This raises the question whether IV–VI semiconductors and other materials exhibit the same "resonant bonding" mechanism as in benzene or graphene, and whether this mechanism should be viewed as a distinct mode of bonding in solids at all.

In this Communication, we provide this missing definition, and thereby clarify the fundamental nature of "resonantly bonded" inorganic solids, including chalcogenide phase-change materials (PCMs). We show that these materials depart considerably from covalent bonding in their behavior, approaching the metallic regime. Yet, they have unique physical properties that arise directly from their special bonding nature and that are different from properties of both metals and covalently bonded solids. We therefore suggest that these materials be referred to as "metavalent" solids or "incipient metals" instead.

We first show that Pauling-like resonant bonding in benzene and its extended analogue, graphite, is very different from that in incipient metals. This difference is so pronounced that a change in terminology appears to be in order. While benzene and graphite have a characteristic, resonating set of π orbitals, they *also* contain strong covalent bonds, typically referred to as the "sp^2" system. The role of this strong "backbone" becomes obvious when studying physical properties such as optical phonon frequencies and their pressure response.

We quantify these properties in **Figure 1**, using first-principles calculations to obtain the frequencies of vibrational modes and the optical properties of prototypical materials. Accurate first-principles calculations based on density-functional theory (DFT) provide a unique opportunity to study diverse materials in the same methodological framework, and the predictive power of such approaches has been exemplified in several high-throughput studies.[8–10] We performed DFT calculations with the PBE functional[20] and norm-conserving pseudopotentials, using ABINIT[21] as detailed in the Supporting Information. Using DFT with this particular functional for such a purpose has been validated against an inelastic X-ray scattering experiment on graphite before,[22] and DFT is likewise widely and successfully applied to PCMs.[23] We are here most interested in the relative change of the phonon frequencies with pressure, which we quantify using the mode-specific Grüneisen parameter γ_i. The latter is a dimensionless quantity, measuring the volume dependence of the frequency ω_i for a given vibrational mode, thereby characterizing the anharmonicity of the interaction potential:

$$\gamma_i = -\frac{V}{\omega_i}\frac{\partial \omega_i}{\partial V}$$

Figure 1a,b shows interesting behavior of GeTe, SnTe, and PbTe. In all of them, ω_i changes strongly with external pressure, leading to very large absolute Grüneisen parameters, $|\gamma_i|$. By exerting pressure on GeTe and SnTe, the structures approach the ideal rocksalt type ($R3m \rightarrow Fm\bar{3}m$ transition). Pressure therefore serves as a direct means to control the extent of the Peierls distortion. While the largest $|\gamma_i|$ are observed near the phase transition, they are very high over the entire pressure range. Furthermore, the phase transition is not a necessary criterion: PbTe takes an undistorted rocksalt structure over the entire pressure range, but it still shows anomalous behavior in its vibrational properties, similar to GeTe and SnTe.

The results in Figure 1b not only reveal that the interaction potential for GeTe, SnTe, and PbTe is very anharmonic, but they explain why these materials have such a low thermal conductivity.[15,24] Large values of γ_i lead to low thermal conductivities of the lattice. As a consequence of this anharmonicity, incipient metals (in particular, PbTe and its chemical derivatives) are promising candidates for thermoelectrics.[15,25]

Furthermore, the structural transition is linked to an electronic instability, reflected in an anomalous increase in the optical dielectric constant (Figure 1c). We note in passing that this divergence is a signature of a quantum critical point. Such a link between structural and electronic anomalies is by far not universally present. For example, ionic ferroelectrics such as non-centrosymmetric oxides show unique structural but not electronic instabilities near the phase transition.

For direct comparison, we computed the same quantities for the textbook cases of Pauling "resonance," namely, benzene and graphite (Figure 1d–f). No similar effect and no anomalous behavior are observed in these materials: the bonding is stiff (reflected in large vibrational frequencies that change only slowly with pressure), presumably due to the rigid sp^2 backbone, and the optical polarizability is lower by orders of magnitude than in incipient metals (note the logarithmic axes in Figure 1e–f). Since the physical properties, as determined by the bonding, are quantitatively and qualitatively different between "resonantly" bonded materials and the above-mentioned chalcogenides, we conclude that the underlying fundamental mechanism must be different as well. What, therefore, is the bonding nature in these chalcogenides, and how can it be described?

To address this problem, we need to go beyond the few examples in Figure 1 and assess a more general dataset. Throughout this paper, we will then construct a "fingerprint" based on well-defined physical properties with which to describe the bonding. Beyond the (optical and vibrational) characteristics already introduced in Figure 1, this task requires additional, quantitative criteria that are applicable to a diverse range of solid-state materials. Among the simplest of these criteria is the distribution of electrons in a material. In textbook examples of covalent solids, say diamond or silicon, electrons are localized near the nuclei and in the bonds between them. In ionic materials, electrons are localized as well, mostly near the anions. By stark contrast, in metals, there are much fewer valence electrons per atomic neighbor, which are therefore delocalized and lead to electronic conductivity. Hence, this quantity provides a first indication of a material's bonding nature. We note that quantum-mechanical studies of charge densities and charge localization in materials can provide a complementary picture, and such work is ongoing; for the scope of the present manuscript, however, we will focus strictly on a property-based definition of bonding. In the following, we assume ideally ordered, defect-free crystals, and experiments that come as close to this limit as possible. While defects and doping may also have a strong influence on the behavior of a material, this influence will be very specific for a given composition.

Another defining feature of a material is its atomic coordination number, which is again linked to the bonding nature. In metallic elements, atoms usually have eight (body-centered cubic) or twelve nearest neighbors (cubic or hexagonal close packing); the structural features are more complex in multicomponent intermetallics, but still nondirectional bonding and large coordination numbers prevail. In "classical" covalent solids, coordination numbers are much lower. This is in accord with the 8–N rule: silicon, an element from the fourth main group ($N = 4$), forms four covalent bonds in its stable structure, whereas phosphorus, from the fifth main group, forms three. **Figure 2** collects such data for several more elements and compounds (see also Table S1, Supporting Information). We first correlate calculated effective coordination numbers (ECoN)[26] with experimentally measured conductivities (Figure 2a). Metals show large values for both (blue), while covalent semiconductors exhibit low to intermediate conductivities and ECoN = 4 for sp^3-bonded materials (such as Si or III–V semiconductors; *red diamonds*) or ECoN ≈ 3 for p-bonded systems (*red squares*). Materials previously referred to as "resonantly" bonded are highlighted in green in this viewgraph. Clearly, they are intermediate between both realms, exceeding the coordination numbers prescribed by the 8–N rule, and approaching the realm of metals. This fits well with the above-mentioned concept of electron deficiency: the number of valence electrons is the same for GeSe and GeTe, but the latter has a much higher ECoN, and therefore a lower valence electron count per atomic neighbor.

The mere observation that materials become more metallic when moving down a group in the Periodic Table is not surprising. However, we find that this pathway is distinctly different in various materials classes. We inspect one of the previously employed indicators for "resonant bonding:"[11,13,14] namely, the fact that they exhibit anomalously high Born effective charges. The latter characterize the sensitivity of a material to lattice distortions, that is, the chemical bond polarisability. We thereby add the fifth and final characteristic property to our emerging definition of metavalent bonding. Figure 2b shows first-principles data for Born effective charges, again correlated with conductivity to trace the covalent → metallic transition. For sp^3-bonded systems (*red diamonds*), including Si, GaAs, and other zincblende-type materials, the conductivities span a wide range from insulating to almost metallic-like behavior (up to ≈10^4 S cm^{-1}), but the Born effective charges increase only very slowly. Similarly, the coordination numbers remain unchanged over a wide range of conductivities (ECoN = 4 for the sp^3 semiconductors C, Si, Ge, and Sn) before jumping rapidly on reaching the regime of classical metals (ECoN = 12 for

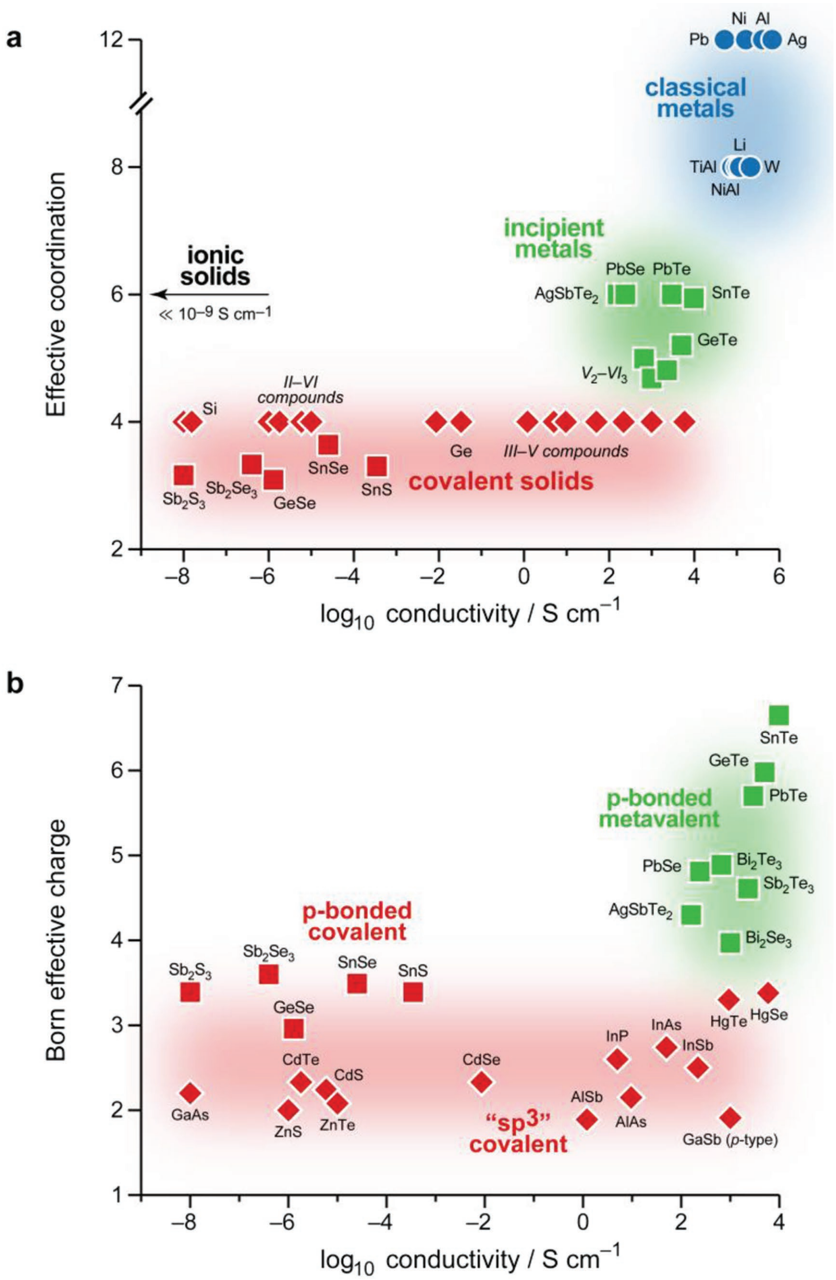

Figure 2. Structural and chemical bond polarizability indicators for a broader set of materials. a) Effective atomic coordination numbers in a range of solids from covalent semiconductors to classical metals. These numbers are plotted versus the tabulated electronic conductivity at or close to room temperature (Table S1, Supporting Information). Materials such as GeTe or PbTe are located between the regime of covalent semiconductors (red) and metals (blue), and we therefore call them "incipient metals" (green). Ionic solids (black) have extremely low intrinsic electronic conductivity, for which experimental data are not normally available; where there is conduction, it is often due to ionic conductivity (the hopping of ions between lattice sites), which is not the topic of this work. An arrow indicates this, exemplarily so for a coordination number of 6 (found, e.g., in the rocksalt type). b) Same for Born effective charges, computed from first principles as detailed in the Supporting Information. These were commonly used as another fingerprint of "resonant bonding." Due to the clear difference from benzene and graphite (Figure 1), we now propose to call this interaction "metavalent" bonding instead. In both viewgraphs, triangles denote "sp^3-bonded" (zincblende-like) crystals whereas squares denote "p-bonded" (orthorhombic or rocksalt-like) systems. Note that the latter terminology refers to the atomic structure only, and p-bonded systems are found to be either covalent or metavalent.

Pb; Figure 2a). This transition looks quite different for many main-group chalcogenides and other p-bonded systems (*red* and *green squares* in Figure 2): the coordination numbers increase gradually even in the presence of a bandgap, incompatible with the 8–*N* rule, and the Born effective charges are atypically high (Figure 2b and Table S1, Supporting Information).

Combining our numerical findings so far, we can now compare the fundamental bonding mechanisms in solids (metallic, covalent, and ionic) to our definition of metavalent bonding. To this end, we compile in **Table 1** all five characteristic identifiers which we have quantified in this work. A comparison of these identifiers reveals that metavalent bonding is a genuine mechanism of bonding in solids and not merely an intermediate (or a combination) of covalent and metallic bonding.

The relevance of metavalent bonding is further emphasized by very recent experimental work which used atom-probe tomography to investigate diverse materials. This study revealed that bonds in metavalent materials break in a unique way, clearly different from both covalently bonded solids and metals.[27] This provides further, independent experimental proof for the presence of a unique bonding mechanism in this materials class.

We finally return to the question of "resonant bonding," completing the conceptual framework derived in this work. Figure 1 established that resonant bonding in benzene and graphite is fundamentally different from metavalent bonding. Our broader numerical study (Figure 2 and Table 1) then characterized metavalent bonding as a distinct "island" between the covalent and metallic regimes—that is, between localized and delocalized bonding. **Figure 3** now combines these findings. Benzene and graphite show both mechanisms (in their sp^2 backbone and π system, respectively), but both are independent from one another (Figure 3b). In contrast, incipient metals attain their unique properties by a delicate balance between both extremes (Figure 3c), tunable by structural distortions (GeTe) or by a small admixture of ionicity (PbTe). This will be investigated further by charge-distribution studies in future work.

Our findings are not only of fundamental interest, but directly relevant for the many practical applications of incipient metals. For example, they provide a new and consistent perspective on the functional principle of PCMs, which are used in data storage[17] or

Table 1. Property-based "fingerprints" to define bonding in inorganic materials. The fingerprint for metavalent solids is a combination of five different identifiers, all of which need to be present in a given material (e.g., NaCl and PbTe have the same structural identifier, but the electronic conductivity in NaCl is extremely low). More specific numerical values are collected in Table S1 in the Supporting Information.

	Ionic (e.g., NaCl, MgO)	Covalent (e.g., Si, GaAs)	Metavalent (e.g., GeTe, PbTe)	Metallic (e.g., Cu, NiAl)
Electronic conductivity (**electrical identifier**)	Very low ($<10^{-8}$ S cm^{-1})	Low to moderate (10^{-8}–10^{2} S cm^{-1})	Moderate (10^{2}–10^{4} S cm^{-1})	High ($>10^{5}$ S cm^{-1})
Effective coordination number[a] (**structural identifier**)	4 (ZnS), 6 (NaCl), 8 (CsCl)	8–*N* rule typically satisfied	8–*N* rule not satisfied	8 (bcc), 12 (hcp/fcc)
Optical dielectric constant ε_∞ (**optical identifier**)	Low (≈2–3)	Moderate (≈5–15)	High (>15)	—[b]
Born effective charges Z^* (**chemical bond polarizability**)	Low (1–2)	Moderate (2–3)	High (4–6)	—[b]
Mode-specific Grüneisen parameters (**anharmonicity**)	Moderate (2–3)	Low (0–2)	High (> 3)	Low (0–2)

[a] For ionic and metallic systems, representative structure types are given, but there are many others especially for multinary systems (e.g., in Zintl phases); [b] This indicator is not normally applicable to the metallic state.

flexible displays.[16] These materials are switched between a crystalline phase ("one bits") and an amorphous phase ("zero bits").[28] The coordination numbers in amorphous PCMs come much closer to obeying the (8–*N*) rule,[29] albeit their complex structures will lead to a visible distribution of ECoNs in a given sample, and cases are known where chemical ordering effects modify this simple view of bonding.[30] Indeed, amorphous PCMs show none of the characteristic identifiers of metavalent bonding listed in Table 1,[13,31] and are instead consistent with the fingerprint of covalent bonding defined there. Upon transition to the crystalline states, the bonding transcends classical covalency: i) the coordination numbers increase, such that the 8–*N* rule is no longer satisfied (Figure 2a); ii) the electronic polarisability rises sharply, which leads to a high optical dielectric constant and thus to the optical contrast between amorphous and crystalline PCMs (Figure 1c); iii) the chemical bond polarizability rises, leading to unusually high Born effective charges (Figure 2b), and, finally, iv) the vibrational properties change strongly, including unusual phonon softening[32] and large mode-specific Grüneisen parameters (Figure 1b). In this, the first point is consistent with the behavior of classical metals (which also exhibit large coordination numbers; Table 1) but the following points ii), iii), and iv) are not. This emphasizes, again, that a combination of properties is needed to define a given bonding mode. We finally note that based on the transition discussed here, one can also characterize these PCMs as "bond-change materials."

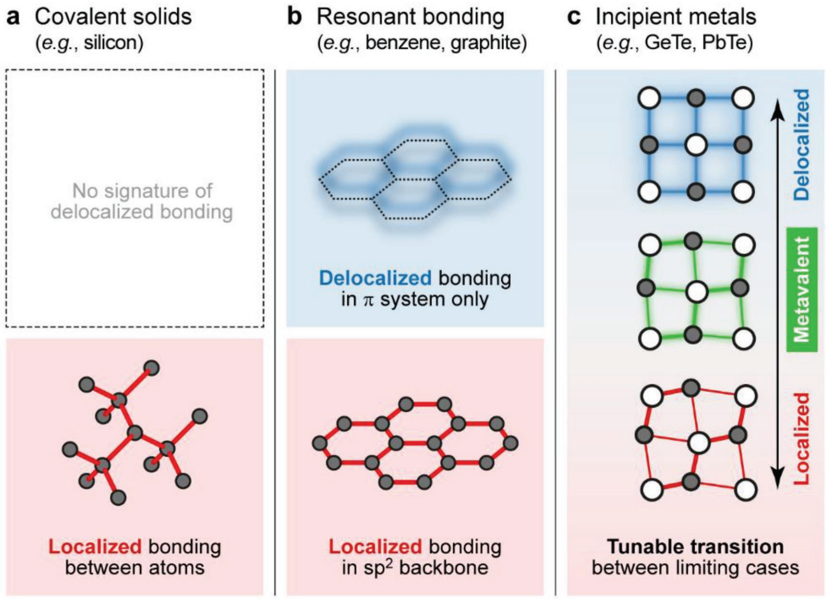

Figure 3. Schematic of bonding in covalent and resonantly bonded systems versus incipient metals. a) Covalent solids, e.g., diamond-type silicon, form strong and localized bonds only. b) In benzene and graphite, both localized sp^2 bonding (red) and delocalized π bonding (blue) exist, but the corresponding orbitals are orthogonal. c) By stark contrast, incipient metals are located between both limiting cases, but with unique properties that are observed only in the intermediate region of metavalent bonding (green). This transition can be tuned, for example, through pressure-induced structural transformations, but the mere presence of a phase transition is not a necessary criterion. For example, PbTe is undistorted but still shows fingerprints of metavalent bonding (Figure 1a–c).

In conclusion, we have identified a unique bonding mechanism in a class of solid-state materials including PCMs. The characteristics of this mechanism are between those of covalency and metallicity, but distinctly different from both. While bonding theories themselves have been under vivid debate at times, we believe that they are most useful when they enable predictions of physical properties. Such predictions have been made with great success in the past, and we expect that the fundamental insight developed in this work will spark new discoveries as well – for example, in the search for new thermoelectrics, as exemplified very recently.[33] Based on a detailed first-principles analysis, we suggest replacing the currently widely used term "resonant bonding" by metavalent bonding for this class of materials, and to call them incipient metals. This avoids ambiguity, as we have shown that metavalent bonding is fundamentally different from "resonant bonding" in graphite and related π-conjugated systems. We expect that incipient metals will provide an ideal playground for studying structure–bonding–property relationships in the future. This will be instrumental for the chemically guided discovery of new materials with unconventional property combinations, including PCMs and new candidates for thermoelectrics or photonics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

M.W. thanks S. Blügel for piquing his interest in the nature of "resonant bonding." The authors are grateful to R. Dronskowski, A. Tchougréeff, F. Ducastelle, R. Lobo, and C. Gatti for ongoing discussions. The authors thank F. Lange, M. Cagnoni, O. Cojocaru-Mirédin, M. Oliveira, and S. Jakobs for help with Figure 2 and remarks on the manuscript, and S. Jakobs for bringing ECoNs to our attention and tabulating the corresponding data. M.W. acknowledges support by the DFG (SFB 917). Moreover, the research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 340698, as well as the Excellence Initiative (Distinguished Professorship). C.B. and J.-Y.R. acknowledge support from the French Research Funding Agency (ANR-15-CE24-0021-05, SESAME). J.-Y.R. acknowledges computational resources provided by the CÉCI funded by the F.R.S.-FNRS under Grant No. 2.5020.11 and the Tier-1 supercomputer of the Fédération Wallonie-Bruxelles, infrastructure funded by the Walloon Region under grant agreement n°1117545.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical bonding, materials design, metavalent bonding, phase-change materials, thermoelectrics

Received: June 14, 2018
Revised: September 4, 2018
Published online:

---

[1] P. Ball, *Nature* **2011**, *469*, 26.
[2] J. K. Burdett, *Chemical Bonding in Solids*, Oxford University Press, New York, Oxford **1995**.
[3] *The Chemical Bond* (Eds: G. Frenking, S. Shaik), Wiley-VCH, Weinheim, Germany **2014**.
[4] S. Alvarez, R. Hoffmann, C. Mealli, *Chem. Eur. J.* **2009**, *15*, 8358.
[5] R. Dronskowski, K. Korczak, H. Lueken, W. Jung, *Angew. Chem., Int. Ed.* **2002**, *41*, 2528.
[6] A. Priimagi, G. Cavallo, P. Metrangolo, G. Resnati, *Acc. Chem. Res.* **2013**, *46*, 2686.
[7] W. G. Zeier, A. Zevalkink, Z. M. Gibbs, G. Hautier, M. G. Kanatzidis, G. J. Snyder, *Angew. Chem., Int. Ed.* **2016**, *55*, 6826.
[8] J. Greeley, T. F. Jaramillo, J. Bonde, I. Chorkendorff, J. K. Nørskov, *Nat. Mater.* **2006**, *5*, 909.
[9] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, O. Levy, *Nat. Mater.* **2013**, *12*, 191.
[10] R. Gautier, X. Zhang, L. Hu, L. Yu, Y. Lin, T. O. L. Sunde, D. Chon, K. R. Poeppelmeier, A. Zunger, *Nat. Chem.* **2015**, *7*, 308.
[11] G. Lucovsky, R. M. White, *Phys. Rev. B* **1973**, *8*, 660.
[12] J. Robertson, K. Xiong, P. W. Peacock, *Thin Solid Films* **2007**, *515*, 7538.
[13] K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, M. Wuttig, *Nat. Mater.* **2008**, *7*, 653.
[14] D. Lencer, M. Salinga, B. Grabowski, T. Hickel, J. Neugebauer, M. Wuttig, *Nat. Mater.* **2008**, *7*, 972.
[15] S. Lee, K. Esfarjani, T. Luo, J. Zhou, Z. Tian, G. Chen, *Nat. Commun.* **2014**, *5*, 3525.
[16] P. Hosseini, C. D. Wright, H. Bhaskaran, *Nature* **2014**, *511*, 206.
[17] V. L. Deringer, R. Dronskowski, M. Wuttig, *Adv. Funct. Mater.* **2015**, *25*, 6343.
[18] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca **1960**.
[19] P. W. Anderson, *Science* **1987**, *235*, 1196.
[20] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
[21] X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côté, T. Deutsch, L. Genovese, P. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah, J. W. Zwanziger, *Comput. Phys. Commun.* **2009**, *180*, 2582.
[22] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, P. Ordejón, *Phys. Rev. Lett.* **2004**, *92*, 075501.
[23] W. Zhang, V. L. Deringer, R. Dronskowski, R. Mazzarello, E. Ma, M. Wuttig, *MRS Bull.* **2015**, *40*, 856.
[24] M. P. Jiang, M. Trigo, I. Savić, S. Fahy, É. D. Murray, C. Bray, J. Clark, T. Henighan, M. Kozina, M. Chollet, J. M. Glownia, M. C. Hoffmann, D. Zhu, O. Delaire, A. F. May, B. C. Sales, A. M. Lindenberg, P. Zalden, T. Sato, R. Merlin, D. A. Reis, *Nat. Commun.* **2016**, *7*, 12291.
[25] K. S. Siegert, F. R. L. Lange, E. R. Sittner, H. Volker, C. Schlockermann, T. Siegrist, M. Wuttig, *Rep. Prog. Phys.* **2015**, *78*, 013001.
[26] G. O. Brunner, D. Schwarzenbach, *Z. Krist.* **1971**, *133*, 127.
[27] M. Zhu, O. Cojocaru-Mirédin, A. M. Mio, J. Keutgen, M. Küpers, Y. Yu, J. Y. Cho, R. Dronskowski, M. Wuttig, *Adv. Mater.* **2018**, *30*, 1706735.
[28] M. Wuttig, N. Yamada, *Nat. Mater.* **2007**, *6*, 824.
[29] A. V Kolobov, P. Fons, A. I. Frenkel, A. L. Ankudinov, J. Tominaga, T. Uruga, *Nat. Mater.* **2004**, *3*, 703.
[30] J.-Y. Raty, W. Zhang, J. Luckas, C. Chen, R. Mazzarello, C. Bichara, M. Wuttig, *Nat. Commun.* **2015**, *6*, 7467.
[31] C. Chen, P. Jost, H. Volker, M. Kaminski, M. Wirtssohn, U. Engelmann, K. Krüger, F. Schlich, C. Schlockermann, R. P. S. M. Lobo, M. Wuttig, *Phys. Rev. B* **2017**, *95*, 094111.
[32] T. Matsunaga, N. Yamada, R. Kojima, S. Shamoto, M. Sato, H. Tanida, T. Uruga, S. Kohara, M. Takata, P. Zalden, G. Bruns, I. Sergueev, H. C. Wille, R. P. Hermann, M. Wuttig, *Adv. Funct. Mater.* **2011**, *21*, 2232.
[33] M. Cagnoni, D. Führen, M. Wuttig, *Adv. Mater.* **2018**, *30*, 1801787.