Chemical Bonding in Chalcogenides: The Concept of Multicenter Hyperbonding

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The precise nature of chemical-bonding interactions in amorphous, and crystalline, chalcogenides is still unclear due to the complexity arising from the delocalization of bonding, and nonbonding, electrons. Although an increasing degree of electron delocalization for elements down a column of the periodic table is widely recognized, its influence on chemical-bonding interactions, and on consequent material properties, of chalcogenides has not previously been comprehensively understood from an atomistic point of view. Here, a chemical-bonding framework is provided for understanding the behavior of chalcogenides (and, in principle, other lone-pair materials) by studying prototypical telluride nonvolatile-memory, “phase-change” materials (PCMs), and related chalcogenide compounds, via density-functional-theory molecular-dynamics (DFT-MD) simulations. Identification of the presence of previously unconsidered multicenter “hyperbonding” (lone-pair–antibonding-orbital) interactions elucidates not only the origin of various material properties, and their contrast in magnitude between amorphous and crystalline phases, but also the very similar chemical-bonding nature between crystalline PCMs and one of the bonding subgroups (with the same bond length) found in amorphous PCMs, in marked contrast to existing viewpoints. The structure–property relationship established from this new bonding-interaction perspective will help in designing improved chalcogenide materials for diverse applications, based on a fundamental chemical-bonding point of view.

Chalcogenide materials exhibit interesting properties for a wide range of applications, ranging from optical[1] or optoelectronic[2] applications, and encompassing applications of topological insulators,[1,4] to low-dimensional materials for electronics[5,6] or thermolectric-generation devices.[7] This broad capability is feasible due to the wide tunability of material properties, depending on chalcogen-atom types, and by their generally wide compositional ranges for glass formation.[8]

Of all the chalcogenides, some tellurides, viz. “phase-change” materials (PCMs), show unique material properties, i.e., ultrafast crystallization rates and large (opto-electronic) property contrasts between amorphous (a-) and crystalline (c-) phases.[9–16] The simultaneous occurrence of both these material properties is rather counterintuitive: the former is supposed to involve small structural differences between a- and c-phases, while the opposite trend would be expected for the latter. Consideration of electron delocalization is also seemingly necessary, in that a single Lewis structure, with bonding and nonbonding electron pairs, is unable fully to describe the electron distributions in both a- and c-PCM phases.[12,13] In order to answer this conundrum, chemical-bonding models, assuming a drastic change in the nature of chemical bonding between the two a- and c-phases, have been proposed,[14–17] and form the current mainstream point of view.

It is useful to classify existing models in terms of the length scale regarding electron delocalization. The resonant-bonding model,[12,14] based on a limited number of Lewis-conforming resonant structures, may be suitable for describing simple crystals with minimal disorder: naturally, structurally disordered a-PCMs are beyond the validity of this model. Likewise, crystals with significant amounts of structural disorder are also difficult to incorporate within this model: PCM systems include metastable, vacancy-containing rocksalt-type Ge$_2$Sb$_2$Te$_5$ (c-GST)[18] (or, more generally, compositions along the pseudo-binary tie-line of GeTe–Sb$_2$Te$_3$[10]), Ag–In–Sb–Te (AIST),[19] I–V–VI$_2$-type compounds,[20] or c-GeTe with vacancies.[21] Although the relevant spatial scale is ill-defined, a measure of electron delocalization with substantial metallic character has been proposed, and termed “metavalent bonding”.[22] A view based on atomic-orbital similarity has also been presented recently.[23] On the other hand, a molecular-orbital (MO) approach, involving notably three-centre, four-electron (3c/4e) interactions, or the valence-bond (VB) theory of hyperbonding, both focus on linear triatomic bonding geometries, and have been successfully adopted to describe hypervalent molecules in Chemistry.[24–26] Formation of linear triatomic bonding geometries has also been recognized in the solid state, in a-GST[13] and c-GeTe–Sb$_2$Te$_3$ alloys,[27] and a signature of electron delocalization within this bonding configuration is found in a-GST.[13] The advantage of this hyperbonding-interaction model over other models is that it can be characteristically linked to microscopic properties of the materials.

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Here, we show that the concept of multicenter, hyperbonding interactions completes the picture of chemical bonding in chalcogenides. Chemical-bonding interactions for \(\alpha\)-/\(\beta\)-PCMs, and associated material properties, are comprehensively elucidated with this model. It is shown that, without invoking any other new type of bonding interaction, property contrasts between \(\alpha\)- and \(\beta\)-phases of PCMs can be understood in terms of their naturally different extents of hyperbonding. This is in dramatic contrast with the existing theory for PCMs.

Figure 1 shows chemical-bonding-indicator data, calculated at the bond critical point (BCP), in simulated models of \(\alpha\)-/\(\beta\)-GST. The trends for \(\alpha\)-GST reveal that the charge density \(\rho_B\),\(^{28}\) electron-localization function \(\text{ELF}_B\),\(^{29}\) negative of the local energy density \(\text{LED}\),\(^{30}\) or negative of the integrated crystal-orbital Hamilton population \(\text{ICOHP}\)\(^{31}\) all increase monotonically with decreasing interatomic distance; this trend may be readily understood, given that the bonding is mainly covalent-like. This perspective is in accord with the observation that covalent-bonding interactions in molecules exhibit negative energy densities (while positive values are found for ionic or intermolecular interactions).\(^{30}\) Other results, however, seemingly render this conclusion uncertain: for instance, charge densities at the BCP \((\approx 0.05 \text{ } e/\text{a}_0^2)\) are rather small to be classified as being associated with purely covalent bonding,\(^{32}\) and the values of \(\nabla^2\rho_B\) are close to zero with a change of sign, an indication of the bonding character being intermediate between covalent (negative \(\nabla^2\rho_B\)) and ionic (positive \(\nabla^2\rho_B\)).\(^{28}\) This presumably results from the additional contribution of metalliclicity, i.e., a tendency for delocalization of valence electrons.

Interestingly, a broad distribution of interatomic distances is also found for metastable rocksalt-type \(\beta\)-GST models (Figure 1), as for \(\alpha\)-GST, due to structural disorder.\(^{11,33}\) An important finding is that nearly all the bonding-character data-points for \(\beta\)-GST exactly overlap with parts of the wider range of data-points for \(\alpha\)-GST (Figure 1a–e). Thus, in this overlap region, bonding characteristics are the same for \(\beta\) and \(\alpha\)-GST for the same bond length. This surprising similarity indicates that interatomic interactions in \(\beta\)-GST are indistinguishable from (some of) those in \(\alpha\)-GST; more precisely, chemical-bonding interactions in \(\beta\)-GST belong to a subgroup of the broad spectrum of interactions existing in \(\alpha\)-GST, but are not a different type of interaction to those present in \(\alpha\)-GST. This finding is in strong contrast to the current consensus that the nature of bonding in \(\alpha\) and \(\beta\)-GST is inherently dissimilar,\(^{11,14}\) which has been the basis for rationalizing the property contrasts in GST. Nevertheless, a meaningful difference exists between the peak positions (i.e., average bond length) of the interatomic-distance distributions: the peak positions for \(\beta\)-GST lie at longer distances.

Figure 1. Chemical-bonding indicators and interatomic-distance distributions for amorphous and crystalline GST models. Data points (blue for amorphous, and red for crystalline, phases) evaluated at the bond-critical point for: a) charge density \((e/\text{a}_0^2)\); b) Laplacian of the charge density \((e/\text{a}_0^2)\); c) local energy density (Hartree/\text{a}_0^3); and e) ELF, where \(e\) is the electron charge and \(\text{a}_0\) is the Bohr radius. d) Data points for ICOHP (eV) are also shown. f) Distribution of interatomic distances for amorphous (top) and crystalline GST models (second from top). The axial bonds (second from bottom) and the remaining ordinary covalent bonds (bottom) in \(\alpha\)-GST models show similar interatomic-distance distributions. Here, all models were generated, and characterized, with PBE exchange-correlation functionals.
interatomic distances compared to those for $a$-GST (Figure 1f).

In $a$-GST, the network structure is conventionally considered to consist of ordinary two-centre/two-electron (2c/2e) covalent bonds (Figure 2a-i). However, since Te lone pairs (LPs) can interact with neighbouring antibonding orbitals (via a hyperbonding interaction), LP delocalization-induced interactions with such antibonding orbitals should also be taken into account (Figure 2a-ii). The involvement of antibonding orbitals was presaged in ref. [13], where the COOP curves, shown in Figure 3e of ref. [13] for axial-bonding Ge and Sb units in $c$-GST, clearly show the involvement of antibonding interactions for (lone-pair) states at the top of the valence band. According to a perturbative treatment for two-electron stabilization interactions,[14] the stabilization energy ($\Delta E_s$) of a LP ($n_A$) via the 3c/4e interaction is inversely proportional to the LP–antibonding orbital energy difference ($\Delta E_{A-BC}$) (Figure 2b), while approximately being proportional to the extent of orbital overlap between the LP than does $E_{BC}$. The interaction (ii) reveals a nontrivial interaction between a LP orbital of A and the antibonding orbital of a B–C bonding pair. A: denotes a LP on an A atom, and -- indicates a weak LP delocalization, while A–B–C denotes the formation of hyperbond pairs among A, B, and C atoms, which can be represented by the two ionic resonant structures, A:B–C and A–B:C. b) A schematic interaction-energy diagram for a LP ($n_A$) stabilization interaction with a nearby antibonding orbital ($\sigma^{*}_{BC}$). c) Variation of ELF values for both short- and long-distance interatomic interactions for (near) linear-bonding configurations found in $a$-GST models. The inset shows data points for interatomic distances rather than ELF values. The data points in the shaded area correspond to the hyperbonds defined in this study. d) The ratio of 3c/4e hyperbonds to the ordinary 2c/2e covalent bonds for different chalcogen-containing amorphous models, depicted as a function of their bandgap (GST: Ge–Sb–Te; GSSe: Ge–Sb–Se; GSS: Ge–Sb–S). Here, the bandgap was defined as the energy difference between the highest occupied and lowest unoccupied Kohn–Sham orbitals.

**Figure 2.** Mechanism of 3c/4e hyperbonding interactions in $a$-GST models. a) 3c/4e bonding configurations for: i,iii) two limiting cases and ii) an intermediate interaction. (i) and (iii) correspond to an insignificant or a strong 3c/4e interaction, resulting in a covalent $\sigma$-bond or hyperbond pair formation, respectively. The LP ($n_A$) and bonding ($\sigma_{BC}$) orbitals are represented by isosurface plots of the maximally localized Wannier functions with light blue (positive) and pink (negative) contours. The antibonding orbital ($\sigma^{*}_{BC}$) is concentrated outside of the bonding region, thereby overlapping more with the LP than does $\sigma_{BC}$. The interaction (ii) reveals a nontrivial interaction between a LP orbital of A and the antibonding orbital of a B–C bonding pair. A: denotes a LP on an A atom, and -- indicates a weak LP delocalization, while A–B–C denotes the formation of hyperbond pairs among A, B, and C atoms, which can be represented by the two ionic resonant structures, A:B–C and A–B:C. b) A schematic interaction-energy diagram for a LP ($n_A$) stabilization interaction with a nearby antibonding orbital ($\sigma^{*}_{BC}$). c) Variation of ELF values for both short- and long-distance interatomic interactions for (near) linear-bonding configurations found in $a$-GST models. The inset shows data points for interatomic distances rather than ELF values. The data points in the shaded area correspond to the hyperbonds defined in this study. d) The ratio of 3c/4e hyperbonds to the ordinary 2c/2e covalent bonds for different chalcogen-containing amorphous models, depicted as a function of their bandgap (GST: Ge–Sb–Te; GSSe: Ge–Sb–Se; GSS: Ge–Sb–S). Here, the bandgap was defined as the energy difference between the highest occupied and lowest unoccupied Kohn–Sham orbitals.
Methods section in the Supporting Information for a detailed definition of hyperbonds). Consequently, bonding interactions in a-GST can be of two different strong types, i.e., ordinary 2c/2e covalent bonds [B–C in Figure 2i] and 3c/4e hyperbonds [A–B and B–C in Figure 2ii], along with a spectrum of weaker 3c/4e interactions [A⋯B in Figure 2ii]. Due to the multicenter nature of these interactions, atomic species can accommodate, with their four s and p atomic orbitals (AOs), up to six bonds and LPs in total, exceeding the ordinary Lewis maximum of four. This therefore addresses the question of how the coordination number in a-GST (and in c-GST) can approach six using their three p orbitals, corresponding to perfect octahedral coordination, and how the total number of bonds and LPs can reach five or six for hypervalent Ge or Sb atoms in a-GST.\[13\]

The proposed LP–antibonding interaction model (Figure 2b) may be validated as follows. First, bond lengths (or ELF\(_0\) values) of 2c/2e bonds (B–C in Figure 2i) increase (or decrease) with the formation of 3c/4e interactions (Figure 2c), which conforms to the hyperbonding concept, as the antibonding level of the B–C bond becomes occupied via this interaction (Figure 2b). Second, the dependence of the hyperbonding tendency on the size of the bandgap of materials (assumed to scale with \(\Delta E_{\text{A-B,C}}\)) shows the expected trend (Figure 2d), i.e., a stronger hyperbonding tendency for materials with smaller bandgaps, i.e., particularly tellurides (a-GST) compared to a-Ge\(_2\)Sb\(_2\)S\(_5\) (a-GSS) and a-Ge\(_2\)Sb\(_2\)Se\(_2\) (a-GSSe). Lastly, the involvement of Te LPs in forming hyperbonds is directly supported by the observation (Figure S5, Supporting Information) that 96% (or 93%) of hyperbonds centred at Ge (or Sb) atoms have at least one, or two, three-fold coordinated Te atoms as ligands, each of which can donate the LP electrons required for the 3c/4e interactions (Figure 2a,b). These percentages are much higher than the overall percentage of three-fold Te atoms (≈50%)\[13\] found in these models. It should be emphasized here that, although the hyperbonds and ordinary covalent bonds were defined when particular tellurides (a-GST) compared to a-Ge\(_2\)Sb\(_2\)S\(_5\) (a-GSS) and a-Ge\(_2\)Sb\(_2\)Se\(_2\) (a-GSSe). Lastly, the involvement of Te LPs in forming hyperbonds is directly supported by the observation (Figure S5, Supporting Information) that 96% (or 93%) of hyperbonds centred at Ge (or Sb) atoms have at least one, or two, three-fold coordinated Te atoms as ligands, each of which can donate the LP electrons required for the 3c/4e interactions (Figure 2a,b). These percentages are much higher than the overall percentage of three-fold Te atoms (≈50%)\[13\] found in these models. It should be emphasized here that, although the hyperbonds and ordinary covalent bonds were defined when

In c-GST, a significant difference with a-GST is that the crystalline symmetry requires Ge and Sb atoms to reside in (distorted) octahedral-ligand environments, allowing for the formation of a maximum of three perpendicular hyperbond pairs, i.e., six bonds. This means that the crystalline structure of metastable c-GST inherently provides conditions favourable for strong hyperbonding, with near-linear alignments of p orbitals. The sharp increase in the percentage of hyperbonds for c-GST, compared to a-GST (Figure 3a), is hence due to this crystal-structure amplification effect. The remaining percentage of non-hyperbonds corresponds to ordinary 2c/2e covalent bonds (ii) in Figure 2a) or weaker 3c/4e bonds (iii) in Figure 2a). This finding, together with the high polar covalency of hyperbonds, is manifested in a higher degree of ionicity in c-GST than in a-GST, due to the charge transfer from Ge and Sb atoms to Te atoms (Figure S1, Supporting Information), with the very pronounced increase of hyperbonds present in c-GST. This reveals an interesting character of hyperbonds that, although their electronegativity difference remains the same, simply switching between a \(\sigma\) (2c/2e) bond and a 3c/4e hyperbond changes the ionicity of the same bond (e.g., the B–C bond in Figure 2a).

It is now clear that the overall bonding difference between a- and c-GST arises from the relative abundances of the bonding types; 2c/2e covalent bonding predominates in a-GST, with a minor proportion of hyperbonds, while dominant multicenter 3c/4e hyperbonding, with a minor proportion of 2c/2e covalent interactions, prevails for c-GST, amplified by its crystal symmetry. LP-delocalization-induced weak 3c/4e interactions [Figure 2a-ii] constitute an essential component of the chemical-bonding interactions in GST, mediating between the two stronger interactions of 2c/2e bonds and of hyperbonds (Figure 2a). LP-delocalization-induced weak 3c/4e interactions could occur for any LP-containing material, but with different interaction strengths, depending on their electronic structures (as indicated in Figure 2b,d), and hence can have a more general importance.

We can link the hyperbonding concept to many material properties. The first to be considered is a salient feature of PCMs, namely the large optical-property contrast between a- and c-phases, e.g., of GST.\[14\] The relationship found here between hyperbonds and Born effective charges (BECs) is the key finding that associates these seemingly unrelated properties (Figure 3a,b). The BEC, averaged over all Ge, Sb, and Te atoms in a-GST (c-GST) models was found to be 2.72 ± 0.98 (6.40 ± 2.30), 3.72 ± 1.76 (8.74 ± 3.60), and −2.57 ± 1.30 (−6.16 ± 3.41), respectively. These values are comparable to those given in a previous report.\[16\] The averaged BEC values for the atomic constituents in a-GST are slightly higher than their nominal ionic charges, but the atomic constituents of c-GST exhibit much higher BEC values. The sharp increase of BEC values from a- to c-GST follows the similar trend of increasing ratios of proportion of hyperbonds to that of ordinary covalent bonds (Figure 3a), indicative of an intimate connection between BEC values and the presence of hyperbonds. To obtain a deeper insight into their relationship, we decomposed the whole distribution of BECs into contributions from atoms belonging to groups of atoms involved in forming a specific number of hyperbonds. As the AOs of each atomic constituent are involved in forming more hyperbond pairs, the atomic constituent tends to show a higher BEC value (Figure 3b). In other words, hyperbonding facilitates a larger BEC than does ordinary covalent bonding: the high sensitivity of electronic polarization to atomic displacements[37] therefore constitutes another characteristic of hyperbonding. Considering the reported proportional relation between BECs and dielectric constants,\[38\] it is the drastically increased number of hyperbonds in c-PCMs that escalates BEC and dielectric-constant values. Thus, crystal symmetry, permitting hyperbonding, is an essential requirement for large optical contrasts between a- and c-phases: the resulting linear atomic alignment hence plays a crucial role. The importance of aligned p orbitals in giving high dielectric constants was also discussed by Huang and Robertson,\[39\] supporting the present conclusion.

The formation, or decomposition, process of hyperbonds, depicted in Figure 2a, provides an additional insight into the dynamical properties of PCMs. The first example of interest is the collective bond-breaking behavior in PCMs found from laser-assisted-evaporation experiments,\[40\] presented as supporting evidence for the existence of metavalent bonding.\[22\] The essential observation identified by us is that the reported
Multiple-event probability (MEP) appears to scale with the hyperbond content. In view of the hyperbonding mechanism and the observations for a-GST, the bonding network of amorphous PCMs can be rather generally described by mixed bonding types, ranging from ordinary covalent bonding to strong hyperbonding (i.e., (i) to (iii) in Figure 2a). Given the capability of atom-probe tomography in differentiating those bonding types, the observations in Ref. [40] of higher MEPs for higher Te contents in a-GeSe$_x$Te$_{1-x}$ (where $x = 0.25, 0.5, 0.75$) may be understood by the stronger hyperbonding tendency of Te atoms. On the other hand, the observation of much higher MEPs for any a-GeSe$_x$Te$_{1-x}$ samples than those for the sp$^3$-bonded (non-hyperbonding) c-InSb, and for the p-bonded (albeit, non-hyperbonding) c-GeSe, can be attributed to the presence, or absence, of multicenter hyperbonding in each material, thereby enabling the differentiation between a- and c-PCMs, as well as between PCMs and non-PCMs, by considering the presence of hyperbonding in each material.

Further associated discussion will be given in the following. In any case, the collective bond-breaking itself can be attributed to the unique response of strongly resonating hyperbonds.

Another finding is that, unlike in crystalline Ge-Sb-S (c-GSS) or Ge-Sb-Se (c-GSSe), interatomic distances in the telluride material, c-GST, show a continuous distribution without any significant gap (or dip) that, otherwise, separates contributions from strong and weak interatomic interactions (Figure 1f; Figure S2, Supporting Information). This is because hyperbonding bridges the gap between strong 2c/2e covalent bonding and weak LP interactions. We therefore postulate that the presence of hyperbonding can provide low-energy-barrier routes for bond formation and breakage: for instance, the transition from an A: + B–C configuration ((ii) in Figure 2a) to an A–B + :C configuration (as a result of the B–C bond breaking from (iii) in Figure 2a, leaving a LP on the C atom) leads to the formation of a new A–B bond at the expense of the B–C bond via an A–B–C hyperbond. This LP-delocalization-assisted formation of hyperbonds, and facile bond switching, is in line with the reported fast valence-charge redistribution and rapid crystallization in this material at high temperatures.[13,17] This behavior is beneficial for fast SET operations for PC memory applications. Conversely, the presence of a fast bond-switching route explains why PCMs are, in general, poor glass formers, which is detrimental to the thermal stability of amorphous PCMs. The decisive role of tetrahedrally bonded dopants in enhancing the thermal stability of amorphous PCMs[41] can be ascribed, from the hyperbonding perspective, to the suppression of these bond-switching processes by the dopants. Finally, a hint of a correlation with phonon anharmonicity is given by the recent observation by Lee et al.[42] that a strong phonon anharmonicity has its fundamental root in the cubic (rocksalt) crystalline structure, enabling a linear alignment of p AOs. The same condition for maximizing hyperbonding suggests that strong anharmonicity may therefore accompany pronounced hyperbonding. It is also interesting to note that strong phonon anharmonicity is often linked to the presence of shallow double-well potentials due to weak Peierls distortions,[33,43] which corresponds to the presence of (weak) hyperbonds.

Now let us compare with other chalcogenides containing different types of chalcogens, as already partly discussed for Figure 2d. On going from GSS to GSSe, and to GST, rather
general trends in bonding characteristics are apparent: i) the difference between GSS and GSSe is relatively small, yet a drastic change occurs from GSSe to GST; and ii) the contrast between a- and c-phases becomes amplified. For instance, a rather small increase of the hyperbond ratio (Figure 3a) occurs from GSS to GSSe, followed by a much larger increment from GSSe to GST, together with the amplifying contrasts between a- and c-models. Although the contrast becomes weaker, basically the same trends are observed for the averaged BECs (Figure 3a). The origin of this distinction between chalcogenides may be described in terms of the factors affecting hyperbonding (Figure 2). The strength of hyperbonding interactions is determined by the energy separation between the energy levels of the interacting LP and antibonding orbitals, along with the extent of spatial overlap between these two orbitals; the lower the energy separation (and/or the larger the overlap of the orbitals), the stronger the interaction. Thus, the prevalence of hyperbonding in tellurides with their valence electrons being more delocalized, rather than in selenides or particularly sulfides, is therefore naturally understood. However, we found that the extent of sp hybridization of the constituent AOs also conveniently discriminates these differences. For the amorphous phases, the trend of sp hybridization, as measured by the distance from the central atom to its LP MLWF centre (WFCLP), is clearly in inverse proportion to the degree of hyperbonding (Figure 3a). The same conclusion is reached for crystalline models (see Supporting Information for details). This sp hybridization, stimulating stereochemical bonding activity of LPs, leads to structural distortion, followed by the breakage of linear atomic alignments in c-GSS, and less so in c-GSSe, i.e., a loss of hyperbonding. The local atomic coordination change involved in the distortion in the crystalline models is found to involve transitions from the initial octahedral coordination to lower coordinated polyhedral units, notably with trigonal-pyramidal geometry, that can be described by the sequential decomposition processes of (iii) → (ii) → (i) in Figure 2a, along the three hyperbonding directions. This is not the case for c-GST (see Figure 3). The trend of stability of multicenter hyperbonding interactions, along with the sustainability of the cubic crystalline form, is, therefore, in increasing order of GSS, GSSe, and GST. In fact, the sp hybridization of AOs itself is detrimental to the hyperbonding, as it diminishes the overlap between AOs compared to the case of three pure p orbitals being involved. The close correlation between the hybridization of AOs, multicenter hyperbonding, and crystal structure therefore rationalizes why most PCMs are tellurides rather than sulfides or selenides. With the same reasoning, it can also be understood why sulfides, or selenides, of binary crystalline IV–VI compounds adopt the black-phosphorus crystalline structure, which is more distorted from its hypothetical cubic rocksalt structure than are tellurides with a rocksalt structure, which is more distorted from its hypothetical cubic rocksalt structure, than are tellurides with a rocksalt structure, which is more distorted from its hypothetical cubic rocksalt structure. This behavior is also well overlap (some of) those for a-GeTe, regardless of the functions used (Figure 4), indicating that chemical-bonding interactions in c-GeTe can also be described as a subgroup of bonding interactions in a-GeTe, as for GST.

Another material system of interest is GeTe, another prototype PCM material. From the hyperbonding point of view (see Methods section in the Supporting Information for more details), long bonds in c-GeTe may be described by a stabilization interaction between Te LPs in one Ge–Te layer and nearby Ge–Te antibonding states in another layer. However, the interaction is not strong (e.g., due to the lack of ideal overlap of relevant orbitals restricted by the crystalline structure), resulting in the formation of alternating one short- and one long-bond layers. A pair of short and long bonds with a linear triratomic bonding geometry can be regarded as an incomplete hyperbond pair, whose configuration lies between cases (ii) and (iii) in Figure 2a. As in GST, chemical-bonding indicators for c-GeTe also well overlap (some of) those for a-GeTe, regardless of the functions used (Figure 4), indicating that chemical-bonding interactions in c-GeTe can also be described as a subgroup of bonding interactions in a-GeTe, as for GST.

We further considered two factors affecting the bonding in c-GeTe, namely pressure and the presence of atomic vacancies. Regardless of pressure or even the presence of cation vacancies (Figure 4 and see the Methods section in the Supporting Information), the chemical-bonding indicators for both types of bonds in c-GeTe have always remained within the range of values found in a-GeTe, as also found for GST. On the other hand, the presence of cation vacancies destroys the local symmetry around a Ge–Te LP, triggering stronger 3c/4e interactions, as revealed by the coupled strengthening, and lengthening, respectively, of long, and short, bonds (Figure 4). As a result, stronger linkages across Ge–Te long-bond layers occur via the process of (ii) → (iii) in Figure 2a. Shortening of a small number of Ge–Te short bonds is also found. Although the overall changes in terms of atomic positions is marginal, the detailed charge redistribution is significant, as indicated by the large disorder in the ELF distribution induced by the introduced vacancies. This disorder is induced as a way of minimizing the system energy following the formation of 3c/4e interactions. Therefore, multicenter hyperbonding interactions provide a useful means of stabilizing defects in c-GeTe, and presumably also in GST. Such vacancy formation induces electron localization near Te atoms, next to the vacancies, (Figure S8, Supporting Information), and the positions of the volumes enclosed by high-ELF isosurfaces closely correspond to the positions of LPs predicted by the valence-shell electron-pair repulsion (VSEPR) theory for each local coordination of the Te atoms, an indication of the formation of stereochemically active LPs accompanying vacancy formation.

The concept of hyperbonding described so far suggests an elementary three-body structural motif in chalcogenides, which consists of either two equal bonds (Figure 2aiii), or a pair of short and long bonds (Figure 2aii), with a perfect, or close to,
linear bonding geometry, respectively. The difference between the three configurations in Figure 2a (i.e., from (i) to (iii)) simply originates from their different strengths of hyperbonding interactions, whose variations are continuous rather than clearly differentiating between the configurations (Figure 2c). This often imposes a difficulty in, e.g., defining coordination numbers of atoms in relevant amorphous chalcogenides, and becomes the origin of severe overlaps between the first and second peaks in pair correlation functions. [13] Also, considering a lack of rigorous justification in disordered material systems, the notion of a “Peierls distortion” for liquid, supercooled liquid, or glassy chalcogenides,[43] which has often been used to describe such linear bonding geometries, can be better rephrased as a “weak hyperbonding interaction” (Figure 2bii), and the presence, and material-dependent abundance, of such geometries in chalcogenide liquids or glasses can be rationalized by the theory of hyperbonding. Another interesting aspect of the hyperbonding model, as stated previously, is that the formation of both weak ((ii) in Figure 2a) and strong ((iii) in Figure 2a) hyperbonds results in the formation of energy levels near the top of the valence band with substantial antibonding character (Figure 2b). Accordingly, such antibonding-character states are observed for amorphous[13] and crystalline[51] chalcogenides where substantial linear triatomic motifs are present. The observation of an overall decrease in the antibonding character with vacancy formation, leading to a stabilization of crystalline cubic GST,[51] can be naturally accounted for in the hyperbonding picture in terms of the reduced total number of hyperbonds with vacancy formation in the cubic crystalline structure.

The clear connections established between hyperbonding interactions, local atomic geometries, and material properties indicate that the structures of materials themselves may therefore provide guidelines for material selection for PCM, or thermoelectric, applications. As emphasised in the previous section, in order to achieve strong hyperbonding interactions in chalcogenides, material structures need to possess crystalline symmetries supporting linear triatomic bonding geometries. (Distorted) rocksalt or rhombohedral crystal structures, for example, satisfy this criterion, whose structures are commonly observed for most of the known phase-change, or thermoelectric, materials: they share a diversity of material properties characteristic of hyperbonding materials, such as high coordination numbers beyond the Lewis octet rule (i.e., the number of bond pairs plus LPs exceeds 4) and high Born-effective charges (or high dielectric constants), along with the aforementioned antibonding character.[10–16,22] The hyperbonding model hence

Figure 4. Chemical bonding in amorphous and crystalline GeTe models. Top row) Effect of pressure (or model density) on: i) the model energy; ii) short and long interatomic distances; iii) chemical-bonding indicators of charge density; iv) energy density; and v) ELF. Middle row) Effect of different exchange-correlation functionals. Short and long interatomic distances are shown with reference to the experimental values, taken from Ref. [46] (i,ii). The charge densities at bond-critical points are shown for amorphous and crystalline GeTe models generated with: iii) SCAN[47]; iv) HSE06-D3[48]; and v) rev-vdW-DF2 exchange-correlation functionals. Bottom row) Effect of cation vacancies on ELF distributions, i) without or ii) with vacancies, and on the chemical-bonding indicators of iii) charge density, iv) energy density, and v) ELF. Ge (blue) and Te (yellow) atoms, with spheres representing vacant sites (magenta), are displayed. The value of the ELF isosurface (cyan) is 0.5. The units of chemical indicators here are the same as in Figure 1.
rationalizes the presence of the preferred crystalline structures for PCM, and thermoelectric, applications. Apart from the distorted rocksalt $c$-GST and rhombohedral $c$-GeTe materials studied here, other relevant material systems may include hexagonal $c$-GST,$^{[29]} c$-AIST,$^{[31]} 1$-$V_1$-$I_2$-type compounds,$^{[32]}$ and crystalline chalcogenides with layered structures, e.g. rhombohedral $V_2$-$V_1$-$I_2$-type crystals of $c$-$Sb_2$Te$_5$, $c$-$Bi_2$Te$_5$, etc.$^{[33]}$ Layered-structure materials with similar compositions, yet whose structures lack such linear structural motifs (such as $c$-$Sb_2$Se$_5$), seldom exhibit these hyperbonding characteristics,$^{[34]}$ consistent with the hyperbonding perspective. In this respect, wider application of the hyperbonding concept for diverse crystals seems to be promising, and is worth future investigation. Narrow bandgaps (Figure 2b), and types of anions which induce minimal sp hybridization of cationic atomic orbitals,$^{[35]}$ are also important factors for such applications. Hence, sp$^3$-bonded glasses, or crystals, with tetrahedral-bonding geometries are representative of non-hyperbonding materials. The hyperbonding model, as outlined in Figure 2, is therefore seemingly able to account for most experimental/simulational observations reported so far, thereby providing a unifying framework for understanding broad classes of chalcogenides, while also being able to suggest useful guidelines for material selection for applications. In particular, the hyperbonding model appears able to establish a clear structure/property relationship, which is absent in other chemical-bonding models proposed so far.

In summary, the concept of multicenter, lone-pair–antibonding hyperbonding interactions extends conventional chemical-bonding theory to give a correct understanding of the electronic structure and properties of chalcogenides. A combination of three-centre/four-electron hyperbonding and ordinary two-centre/two-electron covalent bonding can elucidate the origin of chalcogen-dependent structural differences and material properties associated with heavy Group VI elements. The established connection between chemical bonding, crystal structure, and material properties provides a completely new perspective in understanding, and hence designing, chalcogenide materials for various applications, including phase-change-memory or thermoelectric-generation materials.

Keywords
chalcogenides, chemical bonding, multicenter hyperbonding, phase-change materials

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

Conflict of Interest
The authors declare no conflict of interest.

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