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Comment

Comment on 'Chemical bonding in phase-change chalcogenides'

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Abstract

A recent study published in this journal (*J. Phys.: Condens. Matter* **36** 325706) on *Chemical bonding in phase-change chalcogenides* use several densities-based and localized orbitals-based descriptors to unveil the nature of chemical bond in these systems from their density functional theory wavefunctions. While the adopted tools are appropriate for the envisaged scope, the conclusions on the nature of bonding in chalcogenides appear to result from an incorrect choice of the fragments to which the bonding descriptors are applied. Indeed, the fragments analysed are inconsistent with either the stoichiometry of the crystals they are derived from or the infinite three-dimensional arrangement of bonds in these crystals. Once a consistent choice of fragments is adopted, the chemical bond in the Ge–Te crystal (the most thoroughly discussed phase-change chalcogenide in the previously mentioned paper) is shown to be electron-deficient and partially multicentre in nature, comprising a mixture of 3c–2e and 2c–1e bonds. This result is in striking contrast with the electron-rich and 3c–4e nature of bonding in such a system claimed in Müller *et al* (*J. Phys.: Condens. Matter* **36** 325706) paper. Electron deficiency also characterizes all chemical bonds in crystals of the $(GeTe)_{1-x}(Sb_2Te_3)_x$ pseudobinary system series.

Supplementary material for this article is available online

Keywords: phase-change materials, densities-based and localized orbitals-based descriptors, multicentre bonding, multicentre interactions, *n*-centre electron populations mutual fluctuation, electron-deficient and electron-rich bonds, 3c–2e vs 3c–4e bonds

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1. Introduction

A paper recently published in JPCM on chemical bonding in phase-change chalcogenides [1] concluded that the chemical bonds in these systems are electron rich, multicentre (3c-4e) and 'hypervalent' in nature. This conclusion is in agreement with previous work [2–4] by the same authors of the JPCM paper. However, it contrasts with other, more or less recent, studies that strongly support an electron deficient nature for these bonds [5–7], yet leaving as a challenging question—see below for further discussion—whether these bonds should be classified as multicentre (e.g. 3c–2e) or as conventional 2c–1e bonds in nature [5, 7, 8].

The electron-deficient and electron-rich contrasting visions have a point in common if the latter is analysed using the 3c–4e model of Pimentel and Rundle [9, 10]. In fact, within this simplified orbital-based model, both pictures of bonding eventually involve single-electrons bonds between atoms [1, 5–7] and, therefore, both lead to a number of shared electron pairs in bonding equal to one half. For this reason, according to [1], 3c–2e (or 2c–1e) electron-deficient bonds cannot be discriminated from electron rich 3c–4e bonds on the basis of the 2D maps relating the number of electrons transferred to the number of electron pairs shared between neighbouring atoms. However, it is worth recalling that these specific maps, introduced [11] by supporters of the electron-deficient nature of bonding in chalcogenides, enabled them to single out and identify a class of inorganic solids, including chalcogenides, pnictogens and halide perovskites, which are characterized by an unusual property portfolio [5, 11]. These solids exhibit strong optical absorption, suitable for photovoltaic applications and optical data storage, soft and anharmonic bonds, small effective masses and pronounced levels of static and dynamic disorder, even leading to disorder induced localization [12]. It was also recently shown [6] that these 2D maps are qualitatively similar in nature, regardless of whether they are constructed using densities-based or localized orbitals-based descriptors. This observation suggests that both approaches provide a comparable description of chemical bonding—or at least of the underlying electron transfer (ET) and electron sharing (ES) processes—across all types of systems investigated using these maps. However, in [1], such a vision is contrasted, while emphasizing those cases where significant quantitative differences between the maps obtained with the two kinds of descriptors emerge. According to [1], estimates of ET values and the extent of ES obtained through localized orbitals descriptors are preferable because their values appear more chemically reasonable. Interestingly, in [1] are compared results obtained using both approaches and descriptors that have not yet been adopted in the literature to characterize the chemical bond nature in chalcogenides.

Müller *et al* [1] presents new and potentially interesting results; however, in our view, these results are compromised by incomplete analyses or incorrect assumptions. Several key inconsistencies are overlooked, which, if properly addressed, would likely lead to conclusions that contradict those presented as 'unambiguous' in [1]. Additionally, the discussion of Quantum Theory of Atoms in Molecules ('Bader's theory' [13])-based descriptors in [1] appears to be inappropriate and lacks rigor, compelling readers to adopt a particular interpretation of chemical bonding in phase-change chalcogenides.

This comment seeks to critically evaluate the analysis of the results presented in [1] and the conclusions drawn about chemical bonding in chalcogenides. Where necessary, we have supplemented the findings from [1] with additional results from our own work (see SI, for technical details).

2. Extent and kind of multicentre nature of chemical bonds in phase-change chalcogenides

Two-centre bonding between centres A and B measures the electron delocalization between these centres, that is a *mutual fluctuation* of their electron populations N_a and N_b [14]. These fluctuations are quantified by the covariance of N_a and N_b

$$\mathrm{cov}\left(N_a, N_b\right) = \langle N_a N_b \rangle - \langle N_a \rangle \, \langle N_b \rangle \tag{1}$$

where $<N_a>$, $<N_b>$ and $<N_aN_b>$ are averages of the (instantaneous) values of the electron populations N_a and N_b and of their product. The covariance is easily proved [15] to be intimately related to $\delta\left(A,B\right)$, the electron delocalization indices (DIs) between centres A and B:

$$\mathrm{cov}\left(N_A, N_B\right) = -\delta\left(A,B\right)/2. \tag{2}$$

DIs may also be defined in terms of the electron pair density $\rho_2\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right)$ and represent the number of (fractional) electron pairs delocalized (or shared) between centres A and B [14, 16]. For the sake of simplicity, $\delta\left(A,B\right)$ is multiplied by two to represent the number of electrons shared (ES in the 2D maps referred to above) between centres A and B [11]. However, one must not forget that $\delta\left(A,B\right)$ are obtained in terms of an electron pair distribution and are, therefore, two-electron rather than one-electron quantities as is often referred to [1].

Analogous to the case of the 2-centre bond, a *multicentre* bond implies a *mutual* n-centre *fluctuation* of the electron populations of the n-centres [14]. Such n-centre fluctuations provide a measure of multicentre bonding based on electron distribution statistics and clamped nuclei. When the electron populations of two atoms are statistically independent, the associated delocalization index is zero, indicating that the two atoms are not bonded to one another. Similarly, if the atoms considered for a potential n-centre bonding can be partitioned into two (or more) subsets with independent electron populations, no n-centre bonding is present in such a case [14]. Hence, to classify a bond as either a 3c–2e or a 3c–4e bond, one has first to demonstrate that it is a 3-centre bond, namely that the electron populations of the three involved centres are mutually fluctuating. The most rigorous approach to prove this makes use of the multicentre bond indexes, proposed a long time ago by Ponec *et al* [17, 18] and later extended by Bochicchio *et al* [19]. An alternative—yet related, more general, and more powerful—method involves the use of the complete electron distribution function, which was subsequently

introduced by Angel Pendas *et al* [14, 20]. The multicentre indexes have been formulated either within an exhaustive partitioning of the 3D space into non-overlapping atomic basins [18] (for instance, with regard to the atoms in the context of Bader decomposition of charge density) or within a local, atomic basis partitioning of the *PS* product, where *P* is the so-called charge density bond order matrix and *S* is the overlap matrix [17–19]. Atomic basis partitioning may be performed, for instance, according to a Mulliken-like [19, 21] or Löwdin-like criterion [1, 22, 23]. The use of such criteria in calculating the values of multicentre bond indices causes them to suffer from the same limitations, particularly their basis set dependence, as in the corresponding population analyses [19]. Most of these limitations can be reduced to a considerable extent using multicentre indices formulated within the Bader theory approach [19].

Calculation of multicentre indexes may also be accomplished in the solid state and, analogously to the molecular case, using either Bader's theory-based approach [1] or a local basis formulation [1, 24]. For the former, [1] used Quantum ESPRESSO [25] for the periodic density functional theory (DFT) calculation, followed by a calculation of the Bader's theory atomic domain overlap matrices through the Critic2 code [26], which were used to calculate the multicentre indexes through the solid-state analogous [27–29] of equation 17 of [19]. We implemented a similar approach (see SI) a few years ago, yet we have never used the results we have obtained because we believed they predicted an extremely small multicentre character for bonding in chalcogenides to be truly significant. This is discussed in detail in the following section.

The local-basis approach to solid state multicentre indexes is implemented in the LOBSTER program [23, 30, 31], which projects the Kohn–Sham orbitals (plane-wave basis) produced by the DFT calculation onto a local-orbital basis set. Crystal bond indices (COBIs), including three-centre (and multicentre) bond indices, are calculated by LOBSTER in terms of this local-orbital basis set. Thus, they are dependent on the type of local-orbital basis projection. The average COBIs (integrated crystal orbital index, ICOBI) are local-orbital-based analogs of the multicentre indices in crystals, as defined in Bader's theory. For both indexes, positive values of the three-centre bond index are known to denote the presence of a 3c–2e bond, while negative values denote a 3c–4e bond [18, 19]. Note that any bond in a system with at least three nuclei has a non-zero amount of 3-centre character [14, 19]. Yet, what really matters in defining the bond as a 3-centre one is that its 3-centre character is appreciable [14]. For instance, in the case of water molecules, the Bader's theory 3-centre index is not zero, yet almost completely negligible (0.0028) at the restricted Hartree Fock (RHF) level, and larger but still quite small at the highly electron-correlated level (0.0092, CASSCF wavefunction) [14]. Representative examples of molecular 3c–2e bonds and 3c–4e bonds are the allyl cation and anion, whose Bader's theory 3c indexes were calculated by Bochicchio *et al*. [19] to be as large as 0.409 and −0.111 at the RHF (D95(p, d)) level. The cyclopropenium cation, C_3H_3+, exhibits an extremely large, (0.600), C–C–C 3-centre Bader's theory index, at the DFT/cc-pvTZ level [32]. The Bader's theory index for the B–H_{bridge}–B three-centre bonds in the diborane molecule B_2H_6, which are commonly invoked to explain its electronic structure, is indeed positive as expected from its supposedly 3c–2e nature and small but not negligible (0.069 and 0.049 at the B3LYP/6-311G(d p) and RHF/D95(d,p) levels, respectively) [32]. However, a three-centre bond of similar nature and extent (0.053 at the B3LYP/6-311G(d p) level) was also found in diborane for the BH_2 terminal group as a result of a non-negligible ES between pairs of vicinal H atoms [32]. These secondary interactions and the resulting 3c interactions in the BH_2 terminal groups suggest that chemical bonding in the diborane molecule is more involved than customarily thought [32]. For the Bader's theory B–H–B three-centre index in the B_2H_6 molecular crystal we obtained a slightly larger value of 0.097 relative to the molecular case, using a PBE sol DFT functional that is anticipated to emphasize electron delocalization with respect to a hybrid DFT functional such as B3LYP [33]. In [1] a corresponding value of 0.062 is computed, in qualitative agreement with us. Similarly, our estimate of the three-centre index based on Bader's theory for the purported 3c–4e bond in the XeF_2 molecular crystal is −0.0978, a negative value that closely matches the corresponding estimate of −0.087 reported in [1]. When examining three-centre chemical bonding in prototypical phase-change chalcogenide crystals such as β-GeTe (cubic) and α-GeTe (R3m, trigonal), we find a value for the Te–Ge–Te interaction in β-GeTe (−0.020) that is similar to that reported in [1]. (−0.024). However, we disagree with [1] both in the selection of the three-centre data analysed and the conclusions drawn about the nature of the bonding. Indeed, figure 1 shows unambiguously that only a 4-centre fragment (either Ge–Te–Ge–Te or equivalently Te–Ge–Te–Ge) represents a correct fragment choice to discuss 3-centre bonding in GeTe, since only this minimum-size fragment is consistent with the GeTe crystal stoichiometry and contains the two unique 3c contiguous and linear (or quasi-linear) interactions present in the crystal (Ge–Te–Ge and Te–Ge–Te). Limiting the analysis to only Ge–Te–Ge or to only Te–Ge–Te fragments, provides a compromised understanding of 3-centre interactions in an extended solid such as the GeTe crystal.

Figure 1 includes the three-centre data calculated by us using Bader's theory, as no data for the Ge–Te–Ge interaction are reported in [1]. For both β-GeTe and α-GeTe, the Ge–Te–Ge 3-centre index is positive, while it is negative for Te–Ge–Te. However, the magnitude of the former index (β-phase, 0.076; α-phase, 0.062) is 2–3 times larger than that of the latter (β-phase, | −0.033 |; α-phase, |−0.020|). This observation suggests that, in each of the three infinite linear chains $\{\text{Ge–Te}\}_{n \to \infty}$, the dominant character of 3-centre bonding is electron-deficient—i.e. 3c–2e—rather than electron-rich (3c–4e), as was 'unambiguously' claimed in [1]. This finding is consistent with the average number of electrons present at each centre and the dominant p-character of bonding (*see infra,* paragraph 2, as well as [1]).

Note that, when the centres in the infinite chain are perfectly aligned (β-GeTe), the 3c–2e character of the interaction

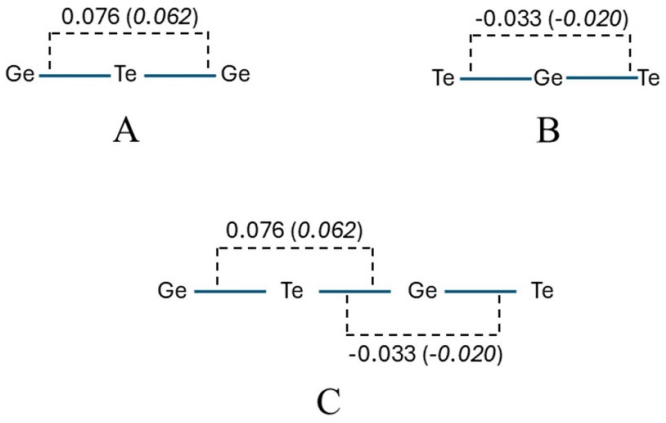

Figure 1. Values of the quantum theory of atoms in molecules (QTAIM, Bader's theory) three-centre bond indexes in β-GeTe (cubic) and α-GeTe (R3m, trigonal) crystals. Top (*A* and *B*): data for two incorrect choices of molecular fragments, both not respecting the stoichiometry of the solid GeTe compound; Bottom (*C*): same three-centre bond indexes as in *A* and *B* fragments but collected for a correct molecular fragment choice. In *A, B* and *C*, data for α-GeTe are reported in parentheses.

further increases relative to the trigonal structure, where the centres are not perfectly aligned (this observation is again consistent with the increase in the p-character of bonding on moving from the trigonal to the cubic structure).

Müller *et al* [1] lists, ICOBI(3), Te–Me–Te (M = Ge or Sb) averaged data, taken from [24], in the GST $(GeTe)_{1-x}(Sb_2Te_3)_x$ pseudobinary system series, namely in β-GeTe ($x = 0$, -0.099), $Ge_3Sb_2Te_6$ ($x = 1/4$, -0.123), $Ge_2Sb_2Te_5$ ($x = 1/3$, -0.130), $GeSb_2Te_4$ ($x = 1/2$, -0.141) and Sb_2Te_3 ($x = 1$, -0.153) systems. In these crystals, the average number of p-electrons on each centre increases from 3 in Ge–Te up to a maximum of 3.6 in Sb_2Te_3, the last element of this series of crystals. Surprisingly, the ICOBI(3) values for Ge-Te-Ge and Ge–Te–Sb (or, equivalently, Sb–Te–Ge) 3c-bonding were all calculated in [24] to be around zero, in sharp contrast with the Bader's theory 3-centre result for the Ge–Te crystal (β- and α-phases) which predicts a 3c index positive and almost three time larger in magnitude for Ge–Te–Ge relative to Te–Ge–Te. We were puzzled by this evident discrepancy and decided to evaluate the 3c- DIs [DI(3)] values for all the systems of the pseudobinary system series named earlier. The results are presented in table 1 for all significant *A–B–C* interactions (where *A, B* and *C* may be Ge, Te, or Sb), along with their associated R_{A-B} and R_{B-C} internuclear distances. For the same systems, the 2c-DI(2) *A–B* values and associated R_{A-B} distances are also listed.

a) could not be computed, because it would require a very large supercell (see SI)

Table 1 shows that the three-centre interaction DI(3) is largely positive for Ge–Te–Ge, and positive in all other cases as well, with DI(3) values of 0.076 for Ge–Te–Ge, 0.029/0.012 for Ge–Te–Sb, and 0.012 for Ge–Te–Te. The Sb–Te–Sb 3c-interactions also have positive DI(3) values, ranging from 0.029 for $x = 1$ to almost zero for $x = 1/2$ [DI(3) = 0.002, implying a negligible 3-centre character]. Sb–Te–Te 3c-interactions have small DI(3) values (0.006) for $x = 1/4$ and $x = 1/3$ or zero value for $x = 1/2$. In the case of Te–Ge–Te 3c-interactions DI(3) values are either moderately negative (-0.033 for $x = 0$ and -0.014 for $x = 1/3$), almost zero (-0.003 for $x = 1/2$) or moderately positive (0.017/0.019 for $x = 1/4$). Te–Sb–Te interactions exhibit either a moderately positive DI(3) value of 0.014, for $x = 1/4$ or a negative value between -0.040 and -0.061 in all other cases.

From the collection of the DI(3) data in table 1, it can be concluded that the DI(3) values for Te–Me–Te (Me = Ge, Sb) are definitely less negative than those reported for ICOBI(3) (Integrated crystal orbitals indices for three atoms) in [24] and in some cases they may even be (significantly) positive. Moreover, for Ge–Te–Ge, Ge–Te–Sb (or equivalently Sb–Te–Ge), the DI(3) values *are not close to zero* as are the ICOBI(3) values reported in [24], *but are instead always positive and in some case quite significantly*. The different descriptions conveyed by DI(3) and ICOBI(3) values would likely deserve investigation by LOBSTER developers. Indeed, while the DI(3) values are only a function of the wavefunction quality, ICOBI(3) values also depend on the way the projection of the local basis has been coded, on the kind of local basis adopted and on the kind of orbitals included in the projections. All these are quite delicate issues that may lead to incorrect results and to previously reported serious discrepancies. A key issue to be verified is whether the overall projection procedure leaves the total electron density invariant locally.

Table 1 shows that bonding in cubic and trigonal GeTe ($x = 0$) has a moderate, yet not negligible three-centre character, and a clearly dominant 3c–2e nature. For $Ge_3Sb_2Te_6$ ($x = 1/4$) the 3c-character is smaller and still of 3c–2e nature for all 3c-interactions. In the case of $Ge_2Sb_2Te_5$ ($x = 1/3$), $GeSb_2Te_4$ ($x = 1/2$) and Sb_2Te_3 ($x = 1$) the 3c-character is negligible or small and of a 3c–2e nature for Ge–Te–Sb, Ge–Te–Te and Sb–Te–Sb ($x = 1$) 3c-bonds, while it is larger in magnitude and of a 3c–4e nature for Te–Sb–Te interactions. Note that we have excluded from our analysis all 3c interactions between non-contiguous atoms, as well as all multicentre interactions beyond the three-centre ones. This is because DI(2), which contributes to the products leading to DI(3), DI(4), etc [15, 19]., becomes increasingly negligible when the interacting atoms are separated by more than two bonds in the analysed systems.

To conclude this paragraph, it is worth mentioning that other models or measures of the multicentre character of *interactions* in chalcogenides and, in general, phase change materials involve nuclear motion in their definition. These models are thus very important for discussing chemical bonding changes upon structural evolution [7, 8, 11, 34, 35], but need not be confused with the notion of *multicentre bonding* which requires the occurrence of mutual fluctuation of the electron populations of the atoms participating in the bond when the nuclei are clamped. In [34]. (one of the coauthors of [1] being the corresponding author of this paper) it was shown that projecting the phononic force-constant tensors for pairs of atoms along different directions and ranges provides a description of the multicentre nature of interactions in rock-salt-type tellurides

Table 1. Quantum theory of atoms in molecules (QTAIM, Bader's theory) 2- and 3-centre delocalization indexes in the entire GST $(GeTe)_{1-x}(Sb_2Te_3)_x$ pseudobinary system [(β-GeTe ($x = 0$), $Ge_3Sb_2Te_6$ ($x = ¼$), $Ge_2Sb_2Te_5$ ($x = 1/3$), $GeSb_2Te_4$ ($x = 1/2$) and Sb_2Te_3 ($x = 1$)] (see SI, for technical details).

2-centre delocalization indexes for the A–B bonds ($R_{e,A-B}$, in Å in parentheses)					
A–B	$x = 0$	$x = ¼$	$x = 1/3$	$x = 1/2$	$x = 1$
Ge–Te	0.435 (3.01)	0.416 (2.96) 0.443 (2.98) 0.463 (2.94)	0.453 (2.95) 0.465 (2.97)	0.298 (3.21) 0.764 (2.82)	
Sb–Te		0.417 (3.16) 0.679 (2.98)	0.427 (3.15) 0.675 (2.99)	0.490 (3.16) 0.537 (3.13) 0.730 (3.01) 0.811 (2.99)	0.444 (3.15) 0.671 (3.00)
Te–Te		0.207 (3.58)	0.197 (3.65)	0.201 (3.69)	
3-centre delocalization indexes for the A–B–C 3c-bonds ($R_{e,A-B}$ and $R_{e,B-C}$, Å in parentheses)					
A–B–C	$x = 0$	$x = ¼$	$x = 1/3$	$x = 1/2$	$x = 1$
Ge–Te–Ge	0.076 (3.01, 3.01)	0.010 (2.98,2.96)	a)		
Ge–Te–Sb		0.012 (2.94, 3.16)	0.029 (2.95, 3.15)	0.016 (3.21, 3.01)	
Ge–Te–Te				0.012 (2.82, 3.69)	
Sb–Te–Te		0.006 (2.98, 3.58)	0.006 (2.95, 3.65)	−0.000 (2.99, 3.69)	
Sb–Te–Sb				0.002 (3.16, 3.13)	0.023 (3.15, 3.15)
Te–Ge–Te	−0.033 (3.01, 3.01)	0.017 (2.98, 2.98) 0.019 (2.94, 2.96)	−0.014 (2.97, 2.95)	−0.003 (3.21, 2.82)	
Te–Sb–Te		0.014 (3.16, 2.98)	−0.040 (3.15, 2.99)	−0.059 (3.16, 2.99) −0.061 (3.13, 3.01)	−0.042 (3,15, 3.00)

and, in general, in phase change materials. This is an excellent measure of the long-range nature of forces and nuclear motions correlations in these systems and has a clear impact on the bonding evolution upon an external perturbation (such as an external pressure, a change in temperature, the action of an electromagnetic field, etc). However, the presence of a *multicentre interaction* does not necessarily imply *multicentre bonding*. We have shown that in cubic and trigonal GeTe, in addition to the occurrence of a multicentre interaction, limited multicentre bonding also occurs. Although less evident, limited signs of multicentre bonding were also present in the remaining members of the $(GeTe)_{1-x}(Sb_2Te_3)_x$ series. The next paragraph further discusses this point in light of the effective number of electrons available for bonding.

3. About the true electron count in chalcogenide bonds

Müller *et al* [1] states that the bonding in both β-GeTe and molecular XeF_2 is electron-rich and similar, involving non-bonding (lone-pair) orbitals. This is in agreement with a series of papers previously published [2, 3, 24, 34] by the same authors of [1]. To further support this claim, [1] reports an observation concerning the frontier orbitals for molecular XeF_2 and those of the Te–Ge–Te and Ge–Te–Ge fragments in β-GeTe. These orbitals were found strikingly similar (see figure 5 of [1]), and are primarily dominated by p-orbital interactions along the internuclear axis. In contrast, s-orbitals play only a very minor role, contributing less than 10% to the total orbital character. Furthermore, the shape of the frontier orbitals of XeF_2 ($2a_{1u}$, $3a_{1g}$, and $3a_{1u}$), as well as that of the frontier orbitals of Te–Ge–Te and Ge–Te–Ge fragments resemble (figure 2 of [1]) the 3c–4e model of Pimentel and Rundle [9, 10]. While such analogies are all true, the analysis made in [1] is incorrect because the considered β-GeTe fragments *are not representative* of the real bonding situation in crystalline β-GeTe. In such a crystal, bonding occurs along three infinite mutually orthogonal linear chains $\{Ge–Te\}_{n \to \infty}$. Assuming that the bonding is 3-centred in nature, each Ge (Te) atom in the crystal is involved in three 3c bonds as a central atom and in six 3c bonds as an outside atom of the 3c bond. This implies that each Ge (Te) atom should use eight electrons for such bonds, assuming that they are of 3c–4e nature, and four electrons, instead, if they are of 3c–2e nature. Namely: in the 3c–4e case, one has 4/3 (electrons/centre) * 3 + 4/3 (electrons/centre) * 6 * 0.5 = 8 electrons involved on average per atom, while in the 3c–2e case one has 2/3 (electrons/centre) * 3 + 2/3 (electrons/centre) * 6 * 0.5 = 4 electrons involved on average per atom. The factor of 0.5 for the six 3c-bonds where the Ge (Te) atom acts as an outside atom of the three-centre interaction serves to avoid double counting of Ge–Te (Te–Ge) interactions already accounted for when the Ge (Te) atom is the central atom of the 3c-interaction.

Considering that there are on average three p valence electrons on each atom and that 3c bonding is essentially p-bonding, it is evident that there are not enough p-valence electrons to realize 3c-4e bonding in β-GeTe crystal. Rather, to be consistent with the average number of electrons available on each Ge (Te) atom, one must necessarily assume an *electron deficient* 3c–2e bonding in such a crystal, implying an average number of four electrons at each centre. The lack of electrons is supplied, for a small amount, by s-orbitals (we know that their contribution is much lower than one electron) and by the fact that the bonding in β-GeTe crystal is not purely 3c–2e in nature, but a combination of 3c–2e and 2c–1e bonding. The latter requires exactly three electrons on average on each Ge (Te) atom, being this atom simultaneously involved in six 2c–1e bonds in a pure 2c–1e model [5].

One may then envisage that along the GST $(GeTe)_{1-x}(Sb_2Te_3)_x$ pseudobinary series, where the average number of p-electrons on each centre increases from three in Ge–Te up to a maximum of 3.6 in Sb_2Te_3, the number of shared electron pairs will progressively increase and overcome that inherent to 2c-1e bonding, while nothing can be said in principle relative to the amount of 3c–2e (or 3c–4e) character of bonding. Table 1 shows that for Ge–Te bonds the average delocalization index increases from 0.435 ($x = 0$), to 0.440 ($x = 1/4$) to 0.459 ($x = 1/3$) up to 0.531 ($x = 1/2$), whereas for Sb–Te it increases from 0.548 ($x = 1/4$) to 0.551 ($x = 1/3$) to 0.558 for $x = 1$, with a notably higher value of 0.642 for Ge1Sb2Te4 ($x = 1/2$). The latter is linked to the breaking of symmetry, as an Sb2Te3 fragment is bound on one side to a Ge atom (3.21 Å) and on the other side to a Te atom (3.69 Å).

The analysis of the amount of 3c–2e (or 3c–4e) character of bonding in the GST $(GeTe)_{1-x}(Sb2Te3)_x$ pseudobinary series has been discussed in the previous paragraph. It is evident, however, that even in the most electron-rich case, $x = 1$, the average number of p electrons on each centre is far below that required to form 3c–4e interactions (in a cubic arrangement, as detailed above for β-GeTe). Therefore, based on the electron count, such an occurrence must be excluded.

The electron deficient nature of bonding in Ge–Te, as demonstrated above, using the same instruments and reasoning used in [1] but considering a correct choice of a Ge–Te fragment in β-GeTe, has already been claimed and supported by several previous studies [5–8]. In particular, the study reported in [5] provides a very convincing demonstration of such a nature, in terms of density of states and domain average Fermi hole [36, 37] analyses of the Ge–Te delocalization index orbital contributions in three crystalline forms of GeTe. More recent studies [7, 8] further corroborate the electron-deficient nature of bonding in Ge–Te and PCM chalcogenides. Based on this evidence, it is difficult to understand why the electron-deficient nature of bonding in crystalline GeTe might still be denied and, instead, its electron-rich nature is claimed. The bonding analysis reported in [1] and made in terms of MO diagrams (figure 5 of [1]) seems to ignore that a fundamental ingredient of this kind of analysis, besides the presence of MOs with suitable shapes, is the number of electrons actually available for filling these MOs.

4. On the comparison of density-based and orbital-based descriptors

In section 3.2 of [1], an analysis is reported on the similarities and differences between the ES vs ET 2D maps obtained in terms of densities-based or localized orbitals-based descriptors. As already pointed out in the introduction, Müller *et al* [1] seem more interested in emphasizing the differences rather than the similarities of these maps and show a clear preference for orbital-based estimates. As correctly argued in [1], the most important cause of the observed discrepancies is related to the different partitioning schemes, one (QTAIM, Bader's theory) being realized in the real space and based on the spatial behaviour of the gradient of the electron density [13] and the other based on assumed (Mulliken's, Löwdin's…) atomic partitioning of the orbital contributions to the ES and ET global values. Bader's partitioning ensures that the atoms bounded by zero-flux $\nabla\rho$ surfaces are open quantum subsystems with well-defined kinetic energy (and total energy at equilibrium) and properties [13], while those defined in terms of an arbitrary partitioning of orbitals contributions represent convenient choices among infinite possibilities. Apart from this deserved premise, statements like 'QTAIM overestimate ET and bond orders' [1] are not warranted. Overestimate relative to what. Can [1] really determine the correct and exact reference for atomic charges and bond orders? Concerning atomic charges, it is obvious (*see infra*) that they cannot summarize the total density in both cases, so none of them may be associated with an exact charge transfer (CT). However, as shown by Meister and Schwarz [38], all methods to evaluate CT, including those based on an atomic charge condensation of the electron and nuclear charge distributions, have a common ionicity principal component. As stated in [38], 'atomic charges are no observables in the strict sense, since they are not measured directly but are deduced from observable quantities on the basis of some more or less arbitrary, more or less simplified (some say oversimplified) model. So, they depend on both the model and on reality'. The factor analysis presented in [38] 'indicates that there is the same real physics behind all these models. However, there is no support for the view that there exists a unique natural scale unit or that only one scale is the *true* one' (quoted from [38]).

Projecting the total density on a finite number of monopole charges, which is equal to the number of nuclei of a system, always introduce errors. The dipole moment of the system is not reproduced at all (if net charges are not explicitly constrained to) and the atomic dipoles need to be considered to correctly reconstruct the dipole moment of the system [39]. Such atomic dipole moments have a clear physical meaning in Bader's partition [13, 39]. For instance, they give rise to a reaction field (partly and generally) opposing that of CT [13, 39]. Their contribution may be of the same order of magnitude as the field due to the CT calculated from the net charges and their analysis provides quite interesting insight, both in the molecular and crystalline cases [39, 40]. Although not generally known, atomic dipoles may also be introduced and defined for orbital based-charges (see page 7 and Table 5 of [39]) and

molecular dipole moments may be exactly reconstructed in this case too if atomic dipoles are included [39]. Clearly, the Bader's net charges and atomic dipoles generally differ from orbital-based charges and dipoles, but both can independently reconstruct the dipole moments calculated as the expectation value of $\boldsymbol{r}$ from the same wavefunction. Therefore, can we really state which is better between the two? No, this would not be a scientific verdict, and we prefer to stay as far away from such kind of not justified statements as possible.

Concerning bond orders, we notice that DIs (the electron sharing used with Bader's partitioning) are defined in terms of the exchange-correlation density, given by the deviation of the electron pair density from the classical product of two independent electron densities [15, 16]. This definition is completely grounded in physics. Can we say that orbital-based bond orders (Wiberg and Mayer's bond orders [41, 42]), which are very much related to DIs for single-determinant wavefunctions, are indeed superior? There are not scientific arguments to prove this. Simple observations based on chemical perception/knowledge may be of interest but not decisive. The correct position and take-home message on the comparison of the electron sharing *vs* electron transfer 2D maps seems us to be that exposed in [6], introducing such a comparison.

5. Conclusions

The present comment analyses in detail a recent paper published in this journal (*J. Phys.: Condens. Matter* **36** 325706) where several densities-based and localized orbitals-based descriptors are used to unveil the nature of chemical bond in phase-change chalcogenides. While the investigative tools adopted in that study are clearly appropriate, the conclusions derived therefrom are significantly compromised by an incorrect choice of the fragments to which the bonding descriptors are applied. The molecular fragments analysed in [1] are inconsistent with either the stoichiometry of the crystals they are derived from or the infinite three-dimensional arrangement of bonds in these crystals. Once a consistent choice of fragments is adopted, the chemical bond in the Ge–Te crystal is shown to be electron-deficient and partially multicentre in nature, being made by a mixture of 3c–2e and 2c–1e bonds. This result is in striking contrast with the electron-rich and 3c–4e nature of bonding in such a system claimed in the commented paper. Electron deficiency was also demonstrated to characterize all the chemical bonds in the crystals of the $(GeTe)_{1-x}(Sb_2Te_3)_x$ pseudobinary system series.

Our conclusions align with the very recent claim that 'in extended solids hypercoordination of electron-rich elements with linear or quasi-linear bonds is only possible for electron-deficient multi-centre bonds' […], since 'the electron-rich multicentre bonds cannot form linear bonds longer than three centres without severely violating the octet rule for the internal atoms of the molecule' [8]. On the other hand, we clearly distinguish in this comment paper between the presence of a multicentre interaction in PCMs and that of the true occurrence of multicentre bonding. The first is related to structural and electronic correlations among bonds upon nuclear displacements, whereas the latter implies a mutual fluctuation of the electron populations of the atoms involved in multicentre bonding at a fixed nuclear configuration. While the first feature is manifestly evident in PCMs and has been reported and studied extensively [7, 11, 34, 35], the second is properly analysed and quantified in the present comment paper. For instance, we show that in cubic and trigonal GeTe, in addition to the occurrence of a multicentre interaction, limited multicentre bonding, in terms of 3c interactions between linearly or quasi-linearly arranged contiguous atoms, also occurs. Although less evident, limited signs of multicentre bonding were also present in the remaining members of the $(GeTe)_{1-x}(Sb_2Te_3)_x$ series.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

The authors declare that they have no affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in the manuscript.

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