

# Vanishing-Harmonicities and Phase-Change Materials

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This article is dedicated to the memory of the late professeur Jacques Friedel (1921–2014) on his 100th birthday

Phase-change material (PCMs) store data using the contrast (electrical or optical) between two phases: a conductive crystalline phase and a weakly conductive amorphous phase. Most PCMs have a distorted octahedral structure. The contrast comes mainly from the electronic structure. In PCMs, a spontaneous symmetry breaking mechanism, the Peierls distortion, transforms the metallic crystalline structure into a lower-density semiconducting structure. In a simple tight-binding model of the covalent bond, the parameters that control this distortion, characterized by a parameter  $\eta$ , are analyzed. The effective interatomic potential  $E(\eta)$  is developed in a Landau-type series in  $\eta$ :  $E(\eta) = E_0 + E_2\eta^2 + E_4\eta^4$ . The PCMs with the largest contrast are those for which the effective potential  $E(\eta)$  of the crystalline phase has a disappearing harmonic contribution ( $E_2 = 0$ ) and a vanishing electronic gap. This is called as an “incipient Peierls distortion.” It coincides with the so-called “incipient metal”. The hardness of the repulsive potential and the number of electrons per atom play an important role. The vibrational properties and the anomalous Grüneisen parameter, specific to PCMs, are also studied.

The storage of binary information requires a system that has two phases with different properties that create a contrast, optical, or electrical. Phase-change materials (PCMs) are compounds of group IV, V, and VI elements, with possibly some additional minor elements, that switch reversibly between a resistive amorphous phase (bit 0) and a conducting crystalline phase (bit 1).<sup>[1–4]</sup>

Tellurium and antimony are key materials in PCM. Antimony is considered as a single element PCM.<sup>[5]</sup>  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  is a reference composition, in addition to GeTe, historically the first.<sup>[1]</sup>

The structure and function of PCMs have been discussed in recent decades, and various models have been suggested over the years: umbrella flipping,<sup>[6]</sup> resonant bonding,<sup>[7]</sup> metavalent bonding,<sup>[3,4]</sup> and Peierls distortion.<sup>[8,9]</sup> The resonant bond theory is historically important, it dates back to Linus Pauling who

introduced, in 1936, the quantum theory in the description of the chemical bond of complex molecules. He suggested that the wavefunctions of the two Kekulé (actually unstable) isomers of benzene with alternating double and single bonds and a threefold symmetry be combined in a linear combination—specific to the quantum theory—with (observed) sixfold symmetry. As with the hydrogen molecule, the resonance energy is the difference between the energy of the unstable Kekulé structure and the bonding linear combination of the two isomers.

The aim herein is to apply the theory of molecular orbitals of Hund and Mulliken in its simplest form (tight binding) to PCMs and analyze to what extent it may describe the original properties of the PCM.

Indeed, PCMs have special features such as two (metastable) structures with different electrical conductivities, a high


dielectric constant  $\epsilon_\infty$ , and a high Born effective charge  $Z^*$ . An important characteristic of PCM is their very large Grüneisen parameter for optical modes, indicating a large anharmonicity which considerably reduces the thermal conductivity of the lattice.<sup>[10,11]</sup>

**Structure:** Most PCMs are alloys of columns IV, V, or VI elements. Their number of  $s$  and  $p$  valence electrons per atom  $N_{sp}$  is in between 4.5 and 5.5. With this number of  $sp$  electrons, the structure is  $p$  bonded with octahedral coordination, possibly deformed, whereas for smaller values ( $N_{sp} \leq 4.5$ ), it is  $sp^3$  bonded and 4-coordinated. In the competition between tetrahedral and octahedral coordination, the latter is favored when  $N_{sp} > 5 - \frac{\epsilon_p - \epsilon_s}{2\beta_{sp^3}}$ ,  $\epsilon_p$  and  $\epsilon_s$  are, respectively, the energies of the  $p$  and  $s$  levels and  $\beta_{sp^3}$  is the resonance integral.<sup>[8]</sup> Throughout this article, we assume that all atoms have octahedral coordination, whether ideal or distorted, in the crystalline or amorphous structure. Sb is a reference element<sup>[5]</sup> as well as its isoelectronic compound GeTe.

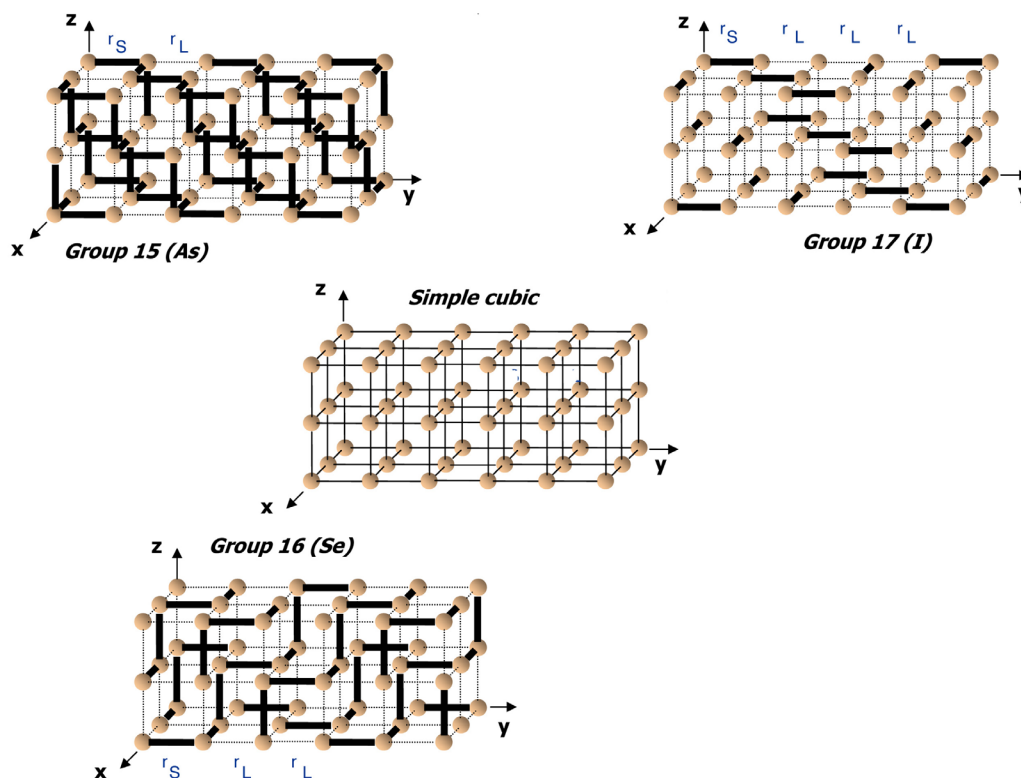
As the three  $p$  orbitals are mutually orthogonal, in a simple cubic or NaCl structure, the problem is decoupled in three 1D problems. Peierls has shown that a 1D lattice with a half-filled band is unstable and leads to a dimerization of the structure, i.e., alternating short and long covalent bonds.<sup>[12–14]</sup> Indeed, an electronic energy is gained by opening a gap at the Fermi level. The total energy is higher (in absolute value) provided that the repulsive energy does not prevent it. If the repulsion is moderate (see further on) in 3D, the cubic structure is unstable and a

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**Figure 1.** Peierls distortion for the columns V (group 15)–VII (group 17) elements of the periodic table. The short distances ( $r_s$ ) are in bold and the long distances ( $r_L$ ) are dotted. Along the  $\langle 100 \rangle$  directions, the sequence is SLSLSL... (dimerization) in group 15 giving corrugated planes parallel to the  $(1\bar{1}1)$  plane. For group 16, one has a sequence SLLSLL... (trimerization) and helical chains with a  $(\bar{1},1,1)$  axis. In group 17, the three directions are no longer equivalent; the structure is made of (001) planes of diatomic molecules.

spontaneous breaking of the symmetry occurs. This was first observed in bismuth.<sup>[15]</sup> **Figure 1** shows how the structure depends on the number of electrons. We discuss the condition of appearance of this distortion in the next section.

*Peierls and the Octet Rule:* In a PCM, the mechanism that transforms a metal into a semiconductor is the Peierls distortion,<sup>[12,13]</sup> a spontaneous symmetry breaking mechanism that makes the material more insulating by opening a gap around the Fermi energy. It is the solid-state analogue of the Jahn–Teller effect.<sup>[14]</sup> By opening a gap, the highest occupied levels, just below the Fermi energy, are pushed down toward more binding energies with a gain of electronic energy.<sup>[16]</sup> In fact, it is sufficient to create a depression of the density of states around the Fermi level to produce an energy gain as the cohesive energy is an integral of the electronic density of states  $n(E)$ .<sup>[8]</sup> In disordered materials (liquid, amorphous), generally, a hollow appears instead of a true gap. The Peierls distortion depends on the volume: by decreasing the volume, the distortion is reduced or even suppressed. Conversely, an increase in volume increases the distortion. As amorphous structures have a larger atomic volume than (ordered) crystalline structures, the Peierls distortion is larger in the amorphous phase, which creates contrast. In addition, Coulombic interactions may play some role in the stabilization of the distortion,<sup>[17]</sup> even a moderate excess charge of trigonal Se or Te closes the gap and the crystal goes back to a metallic state.<sup>[18]</sup>

The octet rule  $Z = 8 - N_{sp}$  is a direct consequence of the Peierls distortion.<sup>[19]</sup>  $Z$ ,  $N_{sp}$ , and  $N_p$  are, respectively, the

coordination number, the number of  $sp$ , and  $p$  electrons. The octet rule can be alternatively written  $Z = 6 - N_p$ . Starting from a hexacoordinated structure (simple cubic or NaCl), the Peierls distortion splits the coordination of 6 in  $6 - N_p$  short (strongly covalent) bonds and  $N_p$  long (weakly covalent) bonds (see **Figure 1**). For example, the coordination of arsenic is 3(+4), of tellurium 2(+4), of iodine 1(+5) (**Table 1**).

Let us start with a 1D Peierls distorted structure (**Figure 2**) which is the [010] row of atoms of group 15 elements (**Figure 1**).

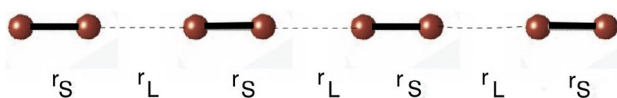
The average distance  $\bar{r}$  and the dimensionless amplitude of the Peierls distortion parameter  $\eta$  are given by

$$\bar{r} = \frac{1}{2}(r_s + r_L) \quad (1)$$

$$\eta = \frac{r_L - r_s}{r_L + r_s} \quad (0 \leq \eta \leq 1) \quad (2)$$

**Table 1.** Coordination numbers of  $p$ -bonded structures with octahedral environment as a function of the number of  $p$  electrons per atom.

Peierls	Nondistorted	Distorted
Coordination $Z$	6	
Coordination (short) $Z$		$6 - N_p$
Coordination (long)		$N_p$



**Figure 2.** A dimerized linear chain.

The local order parameter  $\eta$  varies continuously from 0 to 0.25 or higher, e.g., see Table 4. The PCM have rather low values of  $\eta$ : 0.06 for GeTe and 0.07 for Sb.

$\eta = 0$  corresponds to a periodic linear chain in 1D or a simple cubic structure in 3D.

Let us remark that two opposite behaviors occur regarding the octet rule in alloys (see Table 2).

The lightest elements satisfy the octet rule individually: the coordination number satisfies the octet rule for each atom with its number of  $p$  electrons (e.g., in  $\text{SiO}_2$ ,  $Z_{\text{Si}} = 4$  and  $Z_{\text{O}} = 2$ ). In this case, the bonding mechanism, possibly with  $sp^n$  hybridization, and the local order are similar in crystalline and amorphous materials and the electrical contrast is close to zero. For example, in IV–VI compounds,  $\text{SiO}_2$  has the same tetrahedral local order in the crystalline and amorphous phases, and therefore, similar electrical and optical properties with vanishing contrast:  $\text{SiO}_2$  cannot be used as a memory device.

On the contrary, the heavier elements share their electrons and behave as “average atoms,” i.e., every atom acts as if it has the average number of electrons of the compound and the different components have identical coordination numbers. The covalent bonding is of  $pp\sigma$  nature with an octahedral coordination, possibly distorted so that the octet rule is satisfied for the average number of electrons. For example, GeTe has a coordination 3(+3) for each type of atom. GeTe behaves as if the atoms were Sb. The amplitude  $\eta$  of the Peierls distortion decreases with the atomic number of the elements: the heavier the atoms, the weaker the Peierls distortion. The two opposite behaviors (atomic or global octet rule) are shown in Table 2; the PCMs are close to the diagonal (e.g., GeTe). Finally, for the heaviest elements with a strong repulsion, the distortion disappears and the structure is either of NaCl type (e.g., SnTe, PbSe, PbTe) or simple cubic (Po), the octet rule is no longer observed. This rich behavior is at the origin of the PCM properties. A usable contrast can be produced between amorphous and the crystalline states which have different amplitudes of the Peierls distortion. The variation of the Peierls distortion is the key parameter of PCM efficiency.

**Table 2.** Stoichiometric compositions of the IV–VI compounds. One observes that above the main diagonal (from SiTe to PbO), the octet rule is fulfilled for the individual atoms with a stoichiometry  $\text{AB}_2$  in black. Below the diagonal, in green, the compounds have the stoichiometry AB. The incipient metals lie closest to the diagonal dividing line.<sup>[34]</sup>

	Si	Ge	Sn	Pb
O	$\text{SiO}_2$	$\text{GeO}_2$	$\text{SnO}_2$	$\text{PbO}_2$ , PbO
S	$\text{SiS}_2$	$\text{GeS}_2$	$\text{SnS}_2$	PbS
Se	$\text{SiSe}_2$	$\text{GeSe}_2$ , GeSe	$\text{SnSe}_2$ , SnSe	PbSe
Te	$\text{SiTe}_2$ , SiTe	GeTe	SnTe	PbTe

In summary, from the top to the bottom of the periodic table, one has the sequence: individual octet rule, octet rule in average and undistorted octahedral structure (see Table 2).

Let us finally stress that the respect or not for the octet rule is a difficult question that has no clear-cut answer. Indeed, it relies on the (arbitrary) definition of a cut-off distance. One has to define when two neighboring atoms are bonded (or not) by a covalent bond. A similar difficulty arises in the study of disordered systems (amorphous or liquid) for which the number of nearest neighbors depends on the cut-off distance. As the PCM are weakly Peierls distorted, the discussion on the fulfillment or not of the octet rule is still more difficult as their ratios  $r_L/r_S$  vary continuously in the range [1,1.2] without any gap (Table 4).

One of the consequences of the weak distortion is the displacive rhombohedral-to-rocksalt transition around 700 K for GeTe,<sup>[20]</sup> at 140 K for SnTe,<sup>[21]</sup> and presumably at 2 K for PbTe.

**Energetic Model:** The cohesive properties of covalent materials, including the symmetry breaking mechanism, can be accounted for qualitatively in a simple tight binding<sup>[22,23]</sup> or extended Hückel<sup>[14]</sup> description of the covalent bond.

The total energy is the sum of two terms.

1) An attractive (quantum mechanical) energy due to the resonance between  $p$  orbitals ( $pp\sigma$  bonding). The  $pp\sigma$  resonance widens the  $p$  levels into a  $p$  band of density  $n_p(E)$ . As the  $p$  band is partially filled, an energy gain is obtained: this is nothing but ordinary covalence. We assume that the resonance integrals  $\beta(r)$  decay as the  $q$ -th inverse power of the interatomic separation. Following Harrison,<sup>[24]</sup>  $\beta(r) = \beta_0/r^q$  with  $q = 2$ .

The electronic energy is calculated from the second moment  $\mu_2$  (variance) of the density of states  $n_p(E)$ . For a partially filled band, the electronic energy is related to the bandwidth which is proportional to the square root of second moment  $\mu_2$  of  $n_p(E)$ .<sup>[25]</sup> As  $\mu_2$  is the sum of the squares of the resonance integrals, one gets Equation (3).

2) A repulsive term that is more complex (electrostatic, kinetic, and Pauli contributions). It is approximated by an effective empirical pair interaction. Following Ducastelle<sup>[23]</sup> and Pettifor,<sup>[25]</sup> the repulsive term is approximated by a pairwise additive term.  $E_{\text{rep}}(r) = V_0/r^p$ ,  $p (> q)$  is a parameter that qualifies the strength of the repulsion. The larger the number of inner closed shells, the larger the hardness of the repulsion, the larger the  $p$  value. Consequently,  $p$  increases when going down in the periodic table.

Notice that an exponential decay could also be a valid choice for both terms. The relevant parameters are the dimensionless logarithmic derivatives of the functions decreasing with distance.

We neglect angular variations. The cohesive energy takes the form, in one dimension<sup>[8]</sup>

$$E = \frac{V_0}{2} \left( \frac{1}{r_S^p} + \frac{1}{r_L^p} \right) - \frac{\beta_0}{\sqrt{2}} \sqrt{\frac{1}{r_S^{2q}} + \frac{1}{r_L^{2q}}} \quad (3)$$

where  $V_0$  and  $\beta_0$  are coupling constants of the repulsive and attractive contributions, respectively. This equation is written for a half-filled  $p$  band, with an alternation of short  $r_S$  and long bonds  $r_L$  (Figure 2). The interaction energy (3), involving three atoms is more complex than a sum of pairwise additive contributions. It differs from a harmonic potential with two force

constants. Strong anharmonicities may occur as we will see further on. The two distances  $r_L$  and  $r_S$  are correlated and the dynamical matrix has cross terms. This has important consequences that explains the special properties of PCMs.

If the two interatomic separations  $r_S$  and  $r_L$  are equal, Equation (3) reduces to the classical Mie potential but when the distances are different the energy is no longer pair additive in its attractive part, because of its quantum mechanical nature. The model could be supplemented by an additional ionic contribution, but in PCM, the charge transfer is rather modest and is neglected at this stage.

For a different band filling, the distorted structure is different, as shown in Figure 1; Equation (3) is easily adapted.<sup>[19]</sup>

**Figure 3** shows typical energy landscapes.

Figure 3a corresponds to the situation where  $p > 2q$ , the minimum is on the diagonal ( $r_S = r_L$ ) the stable structure is a linear chain of equally spaced atoms. In that case, the strong repulsive potential prevents dimerisation (e.g., Po, PbTe).

Figure 3b with  $p = 2q$  corresponds to the incipient metal, the middle atom is free to move at zero energy cost between its neighbors along the red central curve because the force constant is zero to first order. It corresponds to the green curve in Figure 5.

In Figure 3c,  $p < 2q$ , i.e., a soft repulsion, a spontaneous symmetry breaking appears. The stable configurations are shown by the first red curves, the two distances  $r_S$  and  $r_L$  (or vice versa) are different (e.g., Sb and GeTe at low  $T$ ).

In summary, Figure 3a corresponds to a metal, Figure 3b to an incipient metal, and Figure 3c to a semiconductor. In the three cases, the bonding is covalent.

In this model, the parameter characterizing the Peierls distortion is the  $p/q$  ratio, i.e., the relative decay rate of the attractive and repulsive terms. The—quantum chemical—attractive term favors the Peierls distortion, whereas the —classical—repulsive term decreases or suppresses it. In 3D, a half-filled  $p$  band is subject to dimerization in the three ( $x, y, z$ ) equivalent directions in space (Figure 1). Sb is a semimetal in the crystalline A7 phase ( $R\bar{3}m$ ) and a semiconductor in the amorphous phase, giving birth to an appreciable contrast in resistivity.<sup>[5]</sup> GeTe is isoelectronic to Sb with similar properties.

Despite its relative simplicity, formula (3) accounts for many properties of covalent systems and it generates rich behaviors.<sup>[8]</sup> It is interesting to note that Peierls had some doubts on the occurrence and usefulness of the mechanism bearing his name.<sup>[13]</sup>

For a given value of  $\bar{r}$ , the cohesive energy  $E$  (Equation (3)) is expanded in power series of  $\eta$ . As the energy is symmetrical in  $\eta$ , only even powers occur in the series expansion, limited to fourth order in  $\eta$  in a Landau-like expansion.

$$E(\bar{r}, \eta) = E_0(\bar{r}) + \alpha(\bar{r})\eta^2 + \gamma(\bar{r})\eta^4 = E_0(\bar{r}) + \Delta E_P \quad (4)$$

where  $\Delta E_P$  is the Peierls energy, i.e., the energy gained by the distortion when  $\alpha < 0$

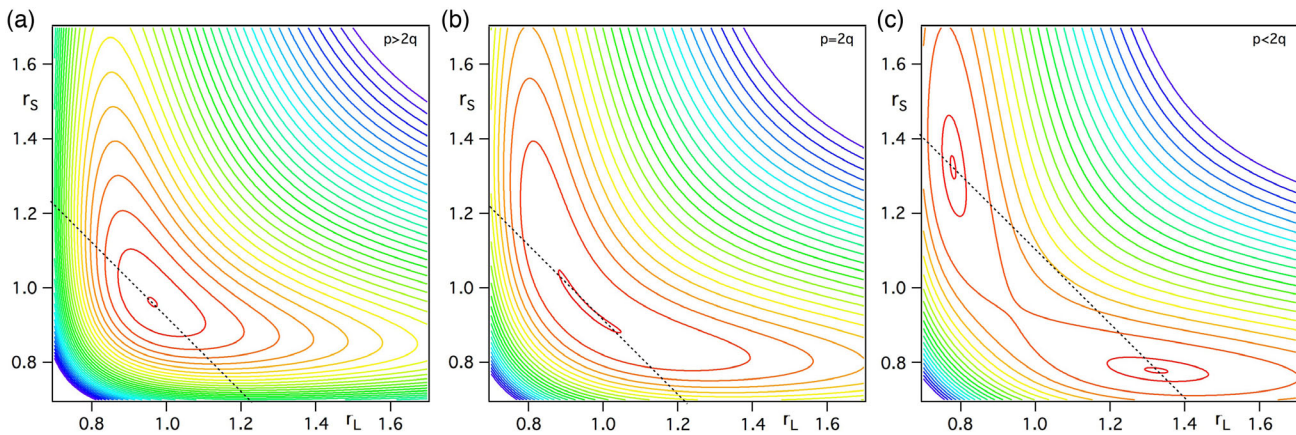
$$\alpha(\bar{r}) = \frac{1}{2} \left[ \frac{V_0}{\bar{r}^p} p(p+1) - \frac{\beta_0}{\bar{r}^q} q(2q+1) \right] \quad (5)$$

and

$$\gamma(\bar{r}) = \frac{1}{12} \left[ \frac{V_0}{\bar{r}^p} p(p+1)(p+2)(p+3) - \frac{1}{2} \frac{\beta_0}{\bar{r}^q} q(2q+1)(6+7q-2q^2) \right] \quad (6)$$

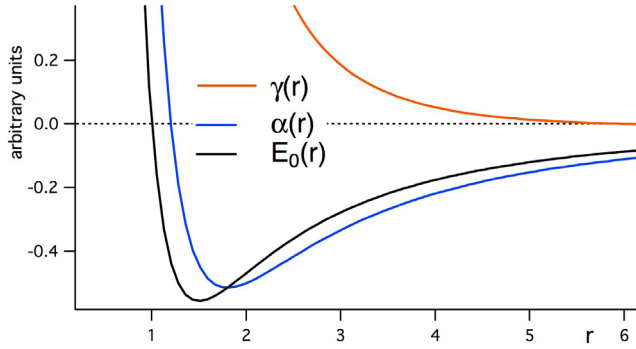
**Figure 4** shows the behavior of  $E_0(r)$ ,  $\alpha(r) = E_2$ , and  $\gamma(r) = E_4$  as a function of the distance  $r$ . In this case,  $\alpha(r)$  is negative at the equilibrium distance (minimum of  $E_0(r)$ ) so that the structure is deformed.  $\gamma(r)$  is positive on a large domain of  $r$ .

The curves of **Figure 5** are the isochoric sections of Figure 3 (dashed line in Figure 3c). Polonium is the only element with a simple cubic structure at room temperature; it corresponds to the black curve of Figure 5. The coefficient  $\alpha(\bar{r})$  determines whether a distortion occurs ( $\alpha < 0$ ) or not ( $\alpha > 0$ ). The quartic term  $\gamma(\bar{r})$  defines, in addition to  $\alpha(\bar{r})$ , the position and amplitude of the distortion. The softer the repulsive potential, the stronger the distortion. The distortion amplitude is obtained from the structural data.<sup>[26,27]</sup> The relation between  $\eta$  and  $r_L/r_S$  is obtained from Equation (2). The  $p/q$  ratio is deduced from the implicit relation (7) (here  $q = 2^{[24]}$ ). The amplitude of the distortion

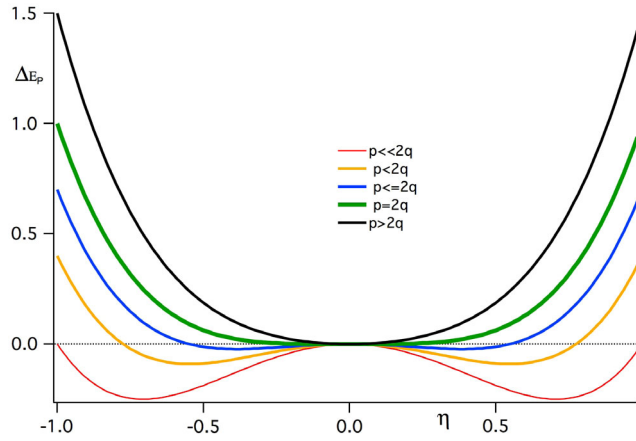


**Figure 3.** a–c) Energy landscapes  $E(r_S, r_L)$ . From left to right : a) undistorted, b) incipient metal, and c) Peierls distorted. The lowest energy configuration corresponds to the first red curve. In the incipient metal (elongated red curve in (b)), the reference point rattles because the force constants vanish to first order. The parameters are chosen such that  $r_S = r_L = 1$  for the undistorted case.





**Figure 4.** Functions  $E_0(r)$ ,  $\alpha(r)$ , and  $\gamma(r)$ .



**Figure 5.** Evolution of the Peierls distortion energy  $\Delta E_p$  as a function of  $\eta$  for different values of the  $p/q$  ratio (increasing from bottom to top). The green curve (incipient metal) corresponds to the cancellation of the harmonic term in Equation (4) ( $E_2 = 0$ ) and  $p = 2q$ . Alternatively, the curves correspond to decreasing volumes (or increasing pressures) from bottom to top.

parameter  $\eta$  at its minimum and the Peierls distortion (PD) energy (see Figure 5) are deduced from (4).

$$\eta = \sqrt{\frac{-\alpha}{2\gamma}} = \frac{\sqrt{6(2q-p)}}{\sqrt{((p+1)(p+2)(p+3) - 0.5(2q+1)(6+7q-2q^2))}} \quad (7)$$

$$\Delta E_p = -\frac{\alpha^2}{4\gamma} \quad (8)$$

The distortion parameter  $\alpha$  is mainly driven by the  $p/q$  ratio. Indeed at the equilibrium distance  $r_e$ , one has

$$\alpha(r_e) = \frac{1}{2} \frac{pV_0}{r_{eq}^p} (p-2q) = E_{coh}(r_e) \frac{pq(p-2q)}{2(p-q)} \quad (9)$$

More generally, starting from (5), for any covalently bonded structure, i.e., for any value of  $p/q$ , there is critical distance  $r_\alpha = \sqrt[p-q]{\frac{p(p+1)V_0}{q(2q+1)\beta_0}} = \sqrt[p-q]{\frac{p+1}{2q+1}} r_e$  below which the structure is undistorted and metallic and above which the structure is Peierls distorted and semiconducting. By varying the volume, one can tune

**Table 3.** Summary of the different cases in the absence of charge transfer.

	Repulsion	Distortion	Conductivity	Potential $E(\eta)$
$p > 2q$	Hard	No distortion	Metal	Harmonic
$p = 2q$	Intermediate	Vanishing distortion	Incipient metal	Zero-harmonic
$q < p < 2q$	Soft	Distortion	Semiconductor	Double well

the electrical resistivity. The amorphous phase having a larger volume than the crystalline phase, its conductivity is lower. Inversely pressure increases conductivity: at a sufficiently high pressure all systems should become metallic (even hydrogen). The transition pressure is strongly dependent on the amplitude of the distortion. The higher the amplitude, the higher the critical pressure. For example, for arsenic, the transition pressure is 25 GPa, 8.5 GPa for antimony, and 2.5 GPa for bismuth. This is quite consistent with the systematic hardening of the repulsive term when going down the periodic table (Table 3).

The relative value of the Peierls distortion energy depends only on the parameters  $p$  and  $q$  and is highly  $\eta$  dependent.

$$\begin{aligned} \frac{\Delta E_p}{E_{coh}} &= \frac{pq[(p+1)(p+2)(p+3) - \frac{1}{2}(2q+1)(6+7q-2q^2)]}{3(p-q)} \eta^4 \\ &= c_4 \eta^4 \end{aligned} \quad (10)$$

The order of magnitude of the factor  $c_4$  can be estimated as follows: if  $q = 2$ ,  $p = 4$ , then  $c_4 \simeq 240$ . This value is relatively independent of the parametrization. For GeTe, the long/short ratio is  $r_L/r_S = 1.12$  with  $\eta = 0.057$  and  $\Delta E_p/E_{coh} = 0.0025$ , and finally  $\Delta E_p \simeq 210$  K as  $E_{coh} \simeq 7$  eV. The order of magnitude is quite compatible with the displacive transition of GeTe from  $R\bar{3}m$  to  $Fm\bar{3}m$  around 700 K.<sup>[20]</sup>

The relation between the Peierls distortion ratio  $\eta$  and the  $p/q$  ratio can be obtained from the implicit equation (Equation (7)) if the structure is distorted. If not, the calculation of  $p$  and  $q$  is much more complex and has to be determined from energy, the interatomic distance and the elastic constants obtained from (3).

The amorphous phase, disordered, is less dense than its crystalline counterpart. To our knowledge, the measures of the densities are rather rare. We estimate a 6 % reduction in density during amorphization,<sup>[28]</sup> i.e., a 2% reduction over the average distances. Our conclusions are insensitive to this arbitrary value.

A closely related effect is the negative thermal expansion (NTE). The temperature weakens or destroys the Peierls distortion and transforms a semiconducting structure into a metallic structure with a density decrease in a temperature domain of about 200 K around the transition temperature<sup>[8]</sup> (Table 4).

**Contrast:** The contrast (optical or electrical) between the two phases is the basis of PCM. The contrast comes mainly from the electronic properties. In addition, it has been shown that the optical contrast is raised by the optical matrix elements that are enhanced in the crystal by aligned rows of resonantly bonded  $p$  orbitals.<sup>[29,30]</sup> As a contrast parameter, we simply take the difference of the electronic gap width  $E_G$  between the crystalline phase and the amorphous phase. The electronic gap is sensitive to the average atomic volume, e.g., in GeSe by comparing the

**Table 4.** Distortion amplitudes,  $\eta$  parameter, and  $p/q$  ratio for various elements and compounds. The distortion amplitude is obtained from the structural data.<sup>[26,27]</sup> The relation between  $\eta$  and  $r_L/r_S$  is obtained from Equation (2). The  $p/q$  ratio is deduced from the implicit relation (7) (here  $q = 2^{[24]}$ ). For nondistorted structures, only a lower bound of the  $p/q$  ratio can be given.

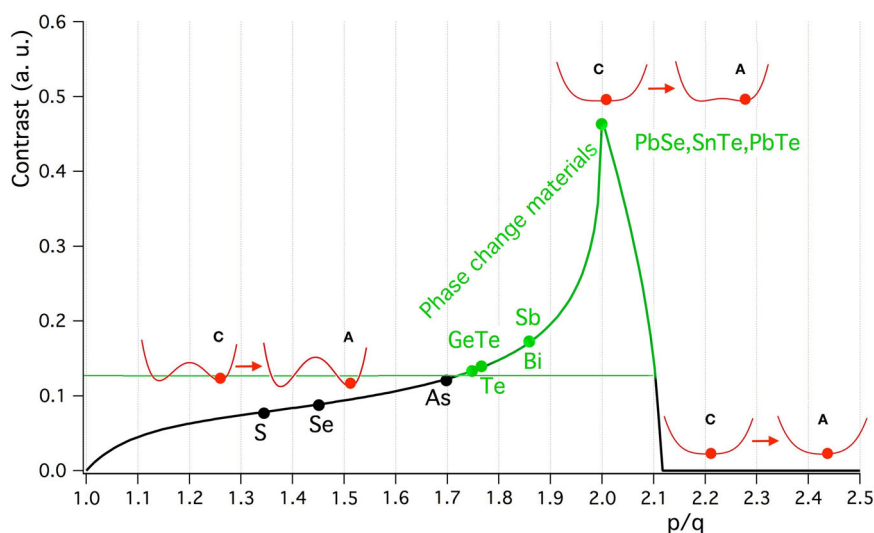
		$r_L/r_S$	$\eta$	$p/q$
As	Crystal	1.24	0.11	1.70
Sb	Crystal	1.15	0.07	1.86
Bi	Crystal	1.15	0.07	1.86
S	Crystal	1.62	0.24	1.35
Se	Crystal	1.49	0.20	1.45
Te	Crystal	1.23	0.10	1.78
GeTe	Crystal	1.12	0.06	1.75
GeTe	Amorphous	1.20	0.09	id.
GeSe	Crystal	1.34	0.14	1.62
GeS	Crystal	1.45	0.18	1.57
SnS	Crystal	1.28	0.12	1.70
SnSe	Crystal	1.26	0.11	1.72
Sb <sub>2</sub> Te	Crystal	1.16	0.07	1.86
Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>	Crystal	1.20	0.09	1.80
SnTe	Crystal	1	0	$\geq 2$
PbS	Crystal	1	0	$\geq 2$
PbSe	Crystal	1	0	$\geq 2$
PbTe	Crystal	1	0	$\geq 2$

different crystalline structures calculated at equilibrium, one finds  $dE_G/dv_{at} = 0.059 \text{ eV}/(\text{u.a.})^3$ .<sup>[17]</sup>

Within our model, the gap width and the contrast are given by

$$E_G = 2|\beta(r_S) - \beta(r_L)| \quad (11)$$

$$\text{Contrast} = E_G^{\text{amorphous}} - E_G^{\text{crystal}}$$



**Figure 6.** Contrast parameter (a. u.) between the crystalline and the expanded amorphous phases as a function of the  $p/q$  ratio. A linear expansion of 2% is assumed upon amorphization. Sketch of the crystalline (C left) and amorphous (A right) potentials  $E(\eta)$ . The PCMs occupy the region above the horizontal green line, along the green thick line. The best PCM corresponds to  $p/q = 2$ , i.e., zero-harmonicity or incipient metal.

where  $\beta(r)$  is the resonance integral between  $p$  orbitals. Indeed, in a dimerised linear chain, with two distances  $r_S$  and  $r_L$ , the band edges are  $-\beta(r_S) - \beta(r_L)$ ,  $-\beta(r_S) + \beta(r_L)$ ,  $\beta(r_S) - \beta(r_L)$ , and  $\beta(r_S) + \beta(r_L)$ .

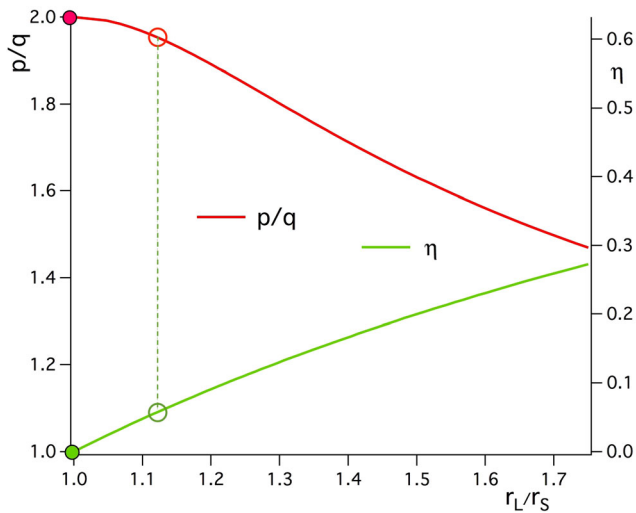
The contrast parameter is shown in **Figure 6** as a function of the  $p/q$  ratio for a 2% distance extension upon amorphization. The highest contrast is achieved when the system shows a vanishing Peierls distortion, i.e., when  $p/q = 2$ . At this value, the electronic gap is just vanishing hence the suggestive name “incipient metal.”<sup>[31]</sup> During amorphization, the volume expansion opens up a gap and creates contrast. In **Figure 6**, the position of the sharp maximum is at  $p/q = 2$ , independently of all other parameters, the width of the curve at half height is roughly proportional to the square of the distance expansion.

Simultaneously, the restoring force in the  $\eta$  parameter vanishes, the vibration mode softens (**Figure 5**, green curve) and the corresponding Grüneisen parameter becomes anomalously large.

This simple theoretical model shows the triple correlation: incipient metal, vanishing Peierls distortion, and anomalous Grüneisen parameter which is characteristic of the PCM. The system is at the borderline between two behaviors: metallic and semiconducting and the switch between them produces the contrast.

The ideal situation for the PCM is a material that achieves the ratio  $p/q = 2$  in the crystalline state (**Figure 6**) with a vanishing Peierls distortion and a zero gap. Then the system becomes Peierls distorted in the amorphous state (**Figure 7**) because of its volume expansion. This maximizes the contrast. In this case, the potential is strongly anharmonic in  $\eta$ . The thermal conductivity of PCMs is very low, even in their crystalline phase, because of the anharmonicity (and also the possible disorder).<sup>[10,32]</sup>

As and Te are PCM candidates in view of their Peierls distortion amplitude but it is difficult to get them amorphous. The borderline case corresponds to a ratio  $r_L/r_S = 1.12$  (upper limit), this is the case of GeTe.<sup>[31]</sup>



**Figure 7.** Plot of  $p/q$  and  $\eta$  versus  $r_L/r_S$ , from Equation (2) and (10). The full circles (left) correspond to the incipient metal with a vanishing electronic gap, the open circles correspond to GeTe.

*Grüneisen Parameter. Effect of Pressure:* One of the most relevant fingerprints of the PCM is the anomalous behavior of the Grüneisen parameter under pressure, very different from tetravalent structures.<sup>[3]</sup> Usually, the dimensionless Grüneisen parameter (Equation (12)) is of the order of unity and varies slowly with pressure. We now consider the variable  $\tilde{\eta} = r_L - r_S = \eta\bar{r}$ , the absolute amplitude (length) of the Peierls distortion instead of the relative amplitude  $\eta$  defined by (2).

For the  $\tilde{\eta}$  mode in 1D, the Grüneisen parameter is defined by

$$\gamma_{\tilde{\eta}} = -\frac{r}{\omega_{\tilde{\eta}}} \frac{\partial \omega_{\tilde{\eta}}}{\partial r} \quad (12)$$

The vibrational frequency of the  $\tilde{\eta}$  mode is  $\omega_{\tilde{\eta}} = \sqrt{\frac{k_{\tilde{\eta}}}{m}}$  where  $k_{\tilde{\eta}}$  is the force constant, related to the curvature of the energy curve in Figure 5 at the minimum.

In the absence of distortion ( $\eta = 0$ ) at zero pressure, in 3D<sup>[33]</sup>

$$\gamma = \frac{p+q}{6} + \frac{1}{6} \quad (13)$$

and for  $p = 4$  and  $q = 2$ ,  $\gamma = 1.17$ .

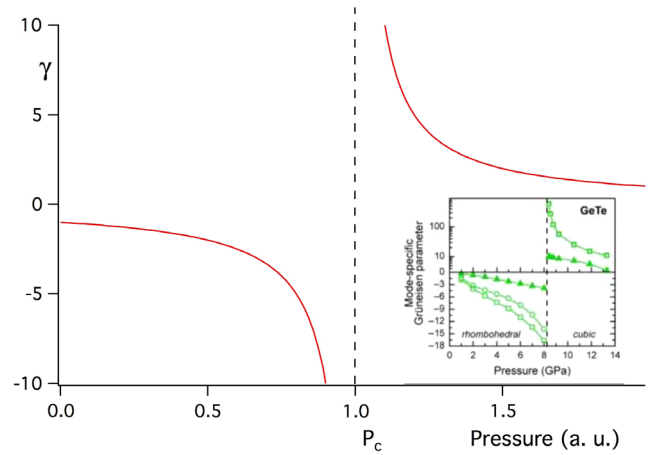
In PCM, the Grüneisen parameter  $\gamma_{\tilde{\eta}}$  varies strongly, it diverges and changes sign at the critical transition pressure  $P_c$ , as shown in the inset of **Figure 8**.

At the equilibrium, the force constant is shown in **Table 5**.

$r_c$  is the distance at which  $\alpha(r) = 0$ , achieved at some critical pressure  $P_c$ . It can be shown that  $\gamma_{\tilde{\eta}}$  varies as

$$\gamma_{\tilde{\eta}} = \frac{C}{P - P_c} \quad (14)$$

in the vicinity of  $P_c$ . Figure 8, shows the anomalous behavior of the Grüneisen parameter of the  $\tilde{\eta}$  mode, in qualitative agreement with the DFT data.<sup>[3]</sup> The divergence of  $\gamma_{\tilde{\eta}}$  at the critical pressure results from the vanishing frequency  $\omega_{\tilde{\eta}}$  consequence of the disappearance of the harmonic term. Could this be related to the



**Figure 8.** Grüneisen parameter  $\gamma$  as a function of pressure (a. u.).  $P_c$  is the transition pressure from distorted to undistorted structure. Inset: Grüneisen parameter of GeTe of the transverse optical mode (adapted from ref. [3]).

**Table 5.** Force constant  $k_{\tilde{\eta}}$  for the various distortion states.

$k_{\tilde{\eta}}$	Structure	$\bar{r}$
$-4\alpha/r^2$	Distorted	$< r_c$
0	0-Harmonic	$= r_c$
$2\alpha/r^2$	Undistorted	$> r_c$

anomalous behavior of the transverse optical phonon mode  $\omega_{LO}$  that are shown in the inset of Figure 8. The DFT calculations using the ABINIT software with the Perdew–Burke–Ernzerhof functional and norm-conserving pseudopotentials, have been done at 0 K in the harmonic approximation:<sup>[3]</sup> only the second derivatives of the energy enter the calculations. The analogy is only apparent. The real situation is more complex and cannot be simply discussed in term of phonons because the phonons are, by definition, related to a harmonic potential, no longer present here at the strict position of an incipient metal (see Figure 5, red curve). In other words, the force is no longer proportional to the displacement, both spring constants (left and right) of an atom vary with the displacement and vanish for the incipient metal. The atom is free to move between its nearest neighbors. As the Grüneisen parameter diverges at  $P_c$  in the model, the thermal conductivity  $\kappa$  vanishes as it varies as  $\gamma^{-2}$ .<sup>[11]</sup> In conclusion, the large Grüneisen parameter and the low value of the thermal conductivity have their origin in the characteristics of the interaction potential (3).

Generally, in 3D solids, the Grüneisen parameter decreases with pressure, to the first approximation like the inverse of the density. Here, pressure decreases the amplitude of the Peierls distortion that vanishes at a given critical pressure  $P_c$  or volume  $V_c$  where the Grüneisen parameter diverges.

*Conclusion:* In summary, the major characteristics of PCMs—their contrast and their anomalous Grüneisen parameter—are explained by a simple covalent model of an octahedrally coordinated structure with a Peierls distortion.

A simple tight-binding model of the  $pp\sigma$  bond with an effective repulsive potential describes the main features of the PCM mechanism.

In conclusion, to obtain an efficient PCM, two necessary conditions must be met: 1. The structure must be octahedral with  $pp\sigma$  bonding. This is achieved by compounds of elements of groups IV, V, and VI with fairly large atomic mass when the number of  $sp$  valence electrons per atom is in the range [4.5, 5.5]. 2. The crystalline structure must have a vanishing (or very small) electronic gap, i.e., it is an incipient metal characterized by a weakly or vanishingly harmonic term  $E_2$  in the energy  $E(\eta)$ . It corresponds to a very weak Peierls distorted structure and, in our model, to a ratio  $p/q \simeq 2$ . It is called “incipient metal” and could also be named “incipient Peierls distortion.”

Of course, these conditions are not sufficient to obtain an operational PCM as other aspects have to be considered, that are outside this model: amorphizability, kinetics of the reversible transformation from the crystalline to the amorphous phase, cyclability.

## Conflict of Interest

The author declares no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

Grüneisen parameters, incipient metals, Peierls distortion, phase-change materials, tight binding

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