

Article

# Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>: Two More Germanides among Polar Intermetallics

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**Abstract:** In this study, two novel  $Lu_5Pd_4Ge_8$  and  $Lu_3Pd_4Ge_4$  polar intermetallics were prepared by direct synthesis of pure constituents. Their crystal structures were determined by single crystal X-ray diffraction analysis:  $Lu_5Pd_4Ge_8$  is monoclinic,  $P2_1/m$ , mP34, a = 5.7406(3), b = 13.7087(7), c = 8.3423(4)Å, β = 107.8(1), Z = 2; Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> is orthorhombic, *Immm*, oI22, a = 4.1368(3), b = 6.9192(5), c = 13.8229(9) Å, Z = 2. The Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> analysed crystal is one more example of non-merohedral twinning among the rare earth containing germanides. Chemical bonding DFT studies were conducted for these polar intermetallics and showing a metallic-like behavior. Gathered results for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> permit to described both of them as composed by  $[Pd-Ge]^{\delta-}$  three dimensional networks bonded to positively charged lutetium species. From the structural chemical point of view, the studied compounds manifest some similarities to the Zintl phases, containing well-known covalent fragment i.e., Ge dumbbells as well as unique *cis*-Ge<sub>4</sub> units. A comparative analysis of molecular orbital diagrams for Ge2<sup>6-</sup> and *cis*-Ge<sup>10-</sup> anions with COHP results supports the idea of the existence of complex Pd–Ge polyanions hosting covalently bonded partially polarised Ge units. The palladium atoms have an anion like behaviour and being the most electronegative cause the noticeable variation of Ge species charges from site to site. Lutetium charges oscillate around +1.5 for all crystallographic positions. Obtained results explained why the classical Zintl-Klemm concept can't be applied for the studied polar intermetallics.

Keywords: polar intermetallics; symmetry reduction; chemical bond

# 1. Introduction

In *RE*–Pd–Ge systems (*RE* = rare earth metal) more than one hundred ternary compounds have already been discovered [1], which have been extensively studied with respect to crystal structure, chemical bonding and physical properties [2-6].

The structures of Ge-rich compounds are characterized by a variety of Ge covalent fragments, with topologies depending both on global stoichiometry and on the nature of the *RE* component. These units are often joined together through Pd atoms, meanwhile the *RE* species are located in bigger channels inside the structure [2,3,7]. The frameworks formed by Pd and Ge atoms have been interpreted as polyanions of general formula  $[Pd_xGe_y]^{\delta-}$  counterbalanced by the rare earth cations, coherently with the definition of these compounds as polar intermetallics [4].



It is interesting to remark that the ternary *RE*–Pd–Ge compounds manifest a tendency to be stoichiometric with ordered distributions of constituents through distinct Wyckoff sites. Moreover, within Pd–Ge fragments, both species have small coordination numbers (usually four or five) with very similar topological distributions of neighbours (tetrahedral coordination or its derivatives). These features may be considered as geometrical traces of a similar chemical role of Pd and Ge. That is why symmetry reduction from certain aristotypes can conveniently depict the distortions related with an ordered distribution of atom sorts. Such analysis has been conducted in the literature for

AlB<sub>2</sub> derivative polymorphs of *RE*PdGe [8] and BaAl<sub>4</sub> derivatives of the *RE*<sub>2</sub>Pd<sub>3</sub>Ge<sub>5</sub> [7,9] family of compounds. In systems where such types of relationships exist, the geometric factor is surely of great importance. Thus, varying *RE*, different polymorphs [8] or even novel compounds may form. As an example, heavy rare earth containing *RE*<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> (*RE* = Er, Tm) [4] and *RE*<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> (*RE* = Ho, Tm, Yb) [3] series of compounds may be cited.

During exploratory syntheses conducted in the Lu–Pd–Ge system in the framework of our ongoing studies on Ge-rich ternary compounds, the Lu representatives of the abovementioned 5:4:8 and 3:4:4 stoichiometries were detected for the first time. In this paper, results on the synthesis and structural characterization/analysis of these new germanides are reported, together with an extensive study of their chemical bonding, including Bader charges, Density of States (DOS) and Crystal Orbital Hamilton Population (COHP) curves as well as Molecular Orbitals (MO) diagrams for Zintl anions composed by Ge.

#### 2. Experimental

## 2.1. Synthesis and SEM-EDXS Characterization

The Lu–Pd–Ge alloys were synthesized from elements with nominal purities >99.9% mass. Lutetium was supplied by Newmet Koch, Waltham Abbey, England, and palladium and germanium by MaTecK, Jülich, Germany.

Different synthetic routes were followed, including arc melting and direct synthesis in resistance furnace. In the latter case, proper amounts of components were placed in an alumina crucible, which was closed in an evacuated quartz ampoule to prevent oxidation at high temperatures, and submitted to one of the following thermal cycles in a resistance furnace:

- (1)  $25 \circ C \rightarrow (10 \circ C/min) \rightarrow 950 \circ C (1 h) \rightarrow (-0.2 \circ C/min) \rightarrow 600 \circ C (168 h) \rightarrow (-0.5 \circ C/min) \rightarrow 300 \circ C \rightarrow \text{furnace switched off}$
- (2)  $25 \degree C \rightarrow (10 \degree C/min) \rightarrow 1150 \degree C (1 h) \rightarrow (-0.2 \degree C/min) \rightarrow 300 \degree C \rightarrow furnace switched off$

A continuous rotation of the quartz ampoule during the thermal cycle was applied. In some cases, the thermal treatment followed arc melting. A scanning electron microscope (SEM) Zeiss Evo 40 (Carl Zeiss SMT Ltd., Cambridge, UK) coupled with a Pentafet Link Energy Dispersive X-ray Spectroscopy (EDXS) system managed by INCA Energy software (Oxford Instruments, Analytical Ltd., Bucks, UK) was used for microstructure observation and phase analysis. For this last purpose, calibration was performed with a cobalt standard. Samples to be analyzed were embedded in a phenolic resin with carbon filler, by using the automatic hot compression mounting press, Opal 410 (ATM GmbH, Mammelzen, Germany), and smooth surfaces for microscopic examinations were obtained with the aid of the automatic grinding and polishing machine, Saphir 520 (ATM GmbH, Mammelzen, Germany). SiC papers with grain sizes decreasing from 600 to 1200 mesh and diamond pastes with particle sizes decreasing from 6 to 1  $\mu$ m were employed for grinding and polishing, respectively.

## 2.2. X-ray Diffraction (XRD) Measurements on Single Crystals and Powder Samples

Single crystals of Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> were selected from suitable samples with the aid of a light optical microscope operated in dark field mode. A full-sphere dataset was obtained in a routine fashion at ambient conditions on a four-circle Bruker Kappa APEXII CCD area-detector diffractometer

equipped by the graphite monochromatized Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation, operating in  $\omega$ -scan mode. Crystals exhibiting metallic luster and glued on glass fibers were mounted in a goniometric head and then placed in a goniostat inside a diffractometer camera. Intensity data were collected over the reciprocal space up to ~30° in  $\theta$  with exposures of 20 s per frame. Semi-empirical absorption corrections based on a multipolar spherical harmonic expansion of equivalent intensities were applied to all data by the SADABS/TWINABS (2008) software [10].

The corresponding CIF files are available in the supporting information material and they have also been deposited at Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, with the following depository numbers: CSD-434226 (Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>) and CSD-434225 (Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>). Selected crystallographic data and structure refinement parameters for the studied single crystals are listed in Table 1. Details regarding the structure solution are discussed in Section 3.2. X-ray powder diffraction (XRPD) measurements were performed on all samples, using a Philips *X'Pert* MPD vertical diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5406$  Å, graphite crystal monochromator, scintillation detector, step mode of scanning). Phase identification was performed with the help of the PowderCell software, version 2.4 [11].

Empirical Formula	Lu <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub>	Lu <sub>3</sub> Pd <sub>4</sub> Ge <sub>4</sub>
EDXS data	Lu <sub>28.6</sub> Pd <sub>24.9</sub> Ge <sub>46.5</sub>	Lu <sub>25.7</sub> Pd <sub>35.0</sub> Ge <sub>39.5</sub>
Space group (No.)	$P2_1/m$ (11)	<i>Immm</i> (71)
Pearson symbol-prototype, Z	<i>mP</i> 34-Tm <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> , 2	<i>oI</i> 22-Gd <sub>3</sub> Cu <sub>4</sub> Ge <sub>4</sub> , 2
a [Å]	5.7406(3)	4.1368(3)
b [Å]	13.7087(7)	6.9192(5)
<i>c</i> [Å]	8.3423(4)	13.8229(9)
$\beta$ (°)	107.8(1)	_
V [Å <sup>3</sup> ]	625.20(5)	395.66(5)
Abs. coeff. ( $\mu$ ), mm <sup>-1</sup>	63.5	60.7
Twin law	$\left[-\frac{1}{2} 0 \frac{1}{2}; 0 - 1 0; \frac{3}{2} 0 \frac{1}{2}\right]$	-
k (BASF)	0.49(1)	-
Unique reflections	2105	404
Reflections I > $2\sigma(I)$ / parameters	1877/87	398/23
GOF on $F^2$ (S)	1.17	1.17
R indices $[I > 2\sigma(I)]$	R1 = 0.0190; wR2 = 0.0371	R1 = 0.0238; wR2 = 0.0869
R indices [all data]	R1 = 0.0247; wR2 = 0.0384	R1 = 0.0242; wR2 = 0.0871
$\Delta \varrho_{\rm fin}$ (max/min), [e/Å <sup>3</sup> ]	2.00/-2.83	2.87/-3.33

**Table 1.** Crystallographic data for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> single crystals together with some experimental details of their structure determination.

#### 2.3. Computational Details

A charge analysis based on Bader's Quantum Theory of Atoms In Molecules (QTAIM) [12], coded in the Vienna Ab-initio Simulation Package (VASP) [13], was used to evaluate the atomic charge populations in the title compounds. Projector augmented waves (PAW) formalism was used, together with Perdew–Berke–Erzenhof parametrization of the exchange-correlation interaction. The recommended PAW sets were used, considering nine valence electrons for Lu ( $6s^25p^65d^1$ ), ten for Pd ( $5s^14d^9$ ), and fourteen for Ge ( $4s^23d^{10}4p^2$ ). An energy cut-off of 600 eV was set for all calculations presented and the default value ( $10^{-5}$  eV) of the energy convergence was used.

The electronic band structures of Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> were calculated by means of the self-consistent, tight-binding, linear-muffin-tin-orbital, atomic-spheres approximation method using the Stuttgart TB-LMTO-ASA 4.7 program [14], within the local density approximation (LDA) [15] of DFT. The radii of the Wigner–Seitz spheres were assigned automatically so that the overlapping potentials would be the best possible approximations to the full potential, and no empty spheres were needed to meet the minimum overlapping criterion.

The basis sets included 6s/(6p)/5d orbitals for Lu with Lu  $4f^{14}$  treated as core, 5s/5p/4d/(4f) for palladium and 4s/4p/(4d)/(4f) orbitals for germanium with orbitals in parentheses being downfolded.

The Brillouin zone integrations were performed by an improved tetrahedron method using a  $20 \times 8 \times 12$  *k*-mesh for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and  $16 \times 16 \times 16$  for Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>.

Crystal Orbital Hamilton populations (COHPs) [16] were used to analyze chemical bonding. The integrated COHP values (*i*COHPs) were calculated in order to evaluate the strengths of different interactions. Plots of DOS and COHP curves were generated using wxDragon [17], setting the Fermi energy at 0 eV as a reference point.

Qualitative MO arguments based on extended Hückel theory (EHT) have been developed with the CACAO package [18,19] and its graphic interface. Even if the EHT model tends to involve the most drastic approximations in MO theory, this one electron effective Hamiltonian method tends to be used to generate qualitatively correct molecular and crystal orbitals [20]. EHT is best used to provide models for understanding both molecular and solid state chemistry, as shown with great success by Roald Hoffmann and others [21].

## 3. Results and Discussion

#### 3.1. Results of SEM-EDXS Characterization

An explorative study of the Ge-rich region of the Lu–Pd–Ge system was conducted by synthesis of some ternary samples with a Ge content >40 at %. The prepared samples are listed in Table 2, together with an indication of the followed synthetic route, as well as the results of SEM/EDXS characterization. Information on phase crystal structure was obtained from X-ray diffraction results.

**Table 2.** Results of SEM/EDXS characterization of the Lu–Pd–Ge samples (> 40 at % Ge) obtained with different synthesis methods/thermal treatments. The highest yield phase in each sample is the first in the list.

No. Overall Composition [at %] Synthesis/Thermal Treatment	Phases	Phase Composition [at %] Lu; Pd; Ge	Crystal Structure	
$1 \\ Lu_{21.4}Pd_{11.2}Ge_{67.4} \\ Arc melting followed by thermal \\ treatment (1)$	Lu <sub>2</sub> PdGe <sub>6</sub> Lu <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> LuPd <sub>0.16</sub> Ge <sub>2</sub> Ge	21.5; 12.1; 66.4 28.6; 25.1; 46.3 31.1; 5.4; 63.5 -; -; -; -;	oS72-Ce <sub>2</sub> (Ga <sub>0.1</sub> Ge <sub>0.9</sub> ) <sub>7</sub> mP34-Tm <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> oS16-CeNiSi <sub>2</sub> cF8-C	
2 Lu <sub>28.9</sub> Pd <sub>24.1</sub> Ge <sub>47.0</sub> Arc melting	Lu5Pd4Ge8 new phase Lu2PdGe6 LuPd0.16Ge2	28.8; 24.8; 46.4 32.4; 28.5; 39.1 21.7; 11.8; 66.5 30.1; 6.9; 63.0	mP34-Tm <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> AlB <sub>2</sub> related oS72-Ce <sub>2</sub> (Ga <sub>0.1</sub> Ge <sub>0.9</sub> ) <sub>7</sub> oS16-CeNiSi <sub>2</sub>	
3 * Lu <sub>30.8</sub> Pd <sub>25.5</sub> Ge <sub>43.7</sub> Direct synthesis with thermal treatment (2)	Lu <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> new phase Ge	28.6; 24.9; 46.5 33.0; 26.8; 40.2 -; -; -;	<i>mP</i> 34-Tm <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> AlB <sub>2</sub> related <i>cF</i> 8-C	
4 * Lu <sub>33.0</sub> Pd <sub>26.0</sub> Ge <sub>41.0</sub> Arc melting followed by thermal treatment (2)	Lu <sub>3</sub> Pd <sub>4</sub> Ge <sub>4</sub> Lu <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> LuPdGe PdGe Ge	25.7; 35.0; 39.5 28.4; 25.1; 46.5 31.9; 34.5; 33.6 0.0; 53.4; 47.6 0.0; 0.0; 100.0	oI22-Gd <sub>3</sub> Cu <sub>4</sub> Ge <sub>4</sub> mP34-Tm <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub> oI36-AuYbSn oP8-FeAs cF8-C	
5 Lu <sub>17.9</sub> Pd <sub>29.0</sub> Ge <sub>53.1</sub> Arc melting	Lu <sub>3</sub> Pd <sub>4</sub> Ge <sub>4</sub> LuPdGe PdGe Ge	26.1; 34.2; 39.7 32.0; 33.5; 34.5 0.0; 52.4; 47.8 0.0; 0.0; 100.0	oI22-Gd <sub>3</sub> Cu <sub>4</sub> Ge <sub>4</sub> oI36-AuYbSn oP8-FeAs cF8-C	

\* Samples from which single crystals were taken.

All samples are multiphase, as it is common for non-annealed alloys belonging to complex ternary systems, Ge is always present, in some cases in small amount. SEM images using the Back-Scattered Electron (BSE) mode are well contrasted, helping to distinguish different compounds, whose compositions are highly reproducible.

Several ternary compounds already known from the literature were detected in the samples, namely Lu<sub>2</sub>PdGe<sub>6</sub>, LuPd<sub>0.16</sub>Ge<sub>2</sub> and LuPdGe [1,2]. For the latter, the *ol*36-AuYbSn structure was confirmed, in agreement with previous single crystal data [8].

A new phase of composition ~Lu<sub>33</sub>Pd<sub>27</sub>Ge<sub>40</sub> was detected in samples 2 and 3; the corresponding X-ray powder patterns could be acceptably indexed assuming a simple AlB<sub>2</sub>-like structure, with a  $\approx$  4.28 and c  $\approx$  3.54 Å. Nevertheless, a deeper structural investigation would be necessary to ensure its crystal structure.

Crystal structures of the new Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> compounds were solved by analysing single crystals extracted from samples 3 and 4, respectively. The obtained structural models, discussed in the following section, were consistent with the measured powder patterns.

#### 3.2. Crystal Structures of Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>

#### 3.2.1. Structural Determination

The Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> crystal selected for X-ray analysis is one more example of non-merohedral twins among germanides. Previously, similar twins were found for Tb<sub>3</sub>Ge<sub>5</sub> [22], Eu<sub>3</sub>Ge<sub>5</sub> [23], Pr<sub>4</sub>Ge<sub>7</sub> [24], La<sub>2</sub>PdGe<sub>6</sub> and Pr<sub>2</sub>PdGe<sub>6</sub> [2]. Based on the preliminary indexing results, the unit cell of the measured crystal might be considered as a base centered orthorhombic one with a = 8.55, b = 21.29 and c = 13.70 Å. The analysis of systematic extinctions suggested the following space groups: Cmc21 (No. 36), C2cm (No. 40) and *Cmcm* (No. 63). It should be mentioned that the average value of  $|E^2-1| = 1.33$ , characterizing the distribution of peak intensities, deviates noticeably from the ideal value (0.968) for centrosymmetric space groups. Frequently, this is an indication of a twinned dataset [25,26]. A charge-flipping algorithm implemented in JANA2006 [27] was used, giving a preliminary structural model with 36 Lu atoms and 96 Ge atoms in the unit cell (*Cmcm* space group). Usually, when scatterers have such remarkable differences in electrons, the charge-flipping algorithm is quick and very efficient in discriminating them. Considering the interatomic distances criterion and U<sub>eq</sub> values, in the successive iteration cycles, Pd atoms were introduced manually by substituting those of Ge, but no improvements were observed. There was no chance to improve this model further because the isotropic thermal displacement parameters showed meaningless values; several additional strong peaks were present at difference Fourier maps located too close to the accepted atom positions; and the R1 value stuck at ca. 10%. Looking for a correct structure solution in other space groups gave no reasonable results.

At this point, a more careful analysis of diffraction spots in reciprocal space was performed using RLATT [10] software. It was noticed that a remarkable number of peaks distributed in a regular way had a small intensity and might be considered as super reflections. Therefore, they were ignored during the indexing procedure, and a four times smaller primitive monoclinic unit cell with a = 5.73, b = 13.70, c = 8.34 Å and  $\beta = 107.8^{\circ}$  was derived. The dataset was newly integrated and semi-empirical absorption corrections were applied by SADABS [10] software. This time, an *m*P34 structural model, containing all the atomic species, was proposed by the charge-flipping algorithm. Even so, the refinement was not satisfactory because some Wyckoff sites manifested partial occupancy and it was not possible to refine the structure anisotropically. It was decided to test the ROTAX [28] algorithm implemented in WinGx [29] and check the possibility of interpreting our crystal as a non-merohedral twin. In fact,

a two-fold rotation along the [101] direction  $\begin{pmatrix} -\frac{1}{2} & 0 & \frac{1}{2} \\ 0 & -1 & 0 \\ \frac{3}{2} & 0 & \frac{1}{2} \end{pmatrix}$  was proposed as a twin law obtaining

a good figure of merit.

To check this hypothesis and refine the collected data as accurately as possible, the initially selected batch of ca. 1000 reflections (comprising those of weak intensity considered as super reflections) was separated into two groups with the help of the CELL\_NOW [10] program, suggesting the same twin law for the two monoclinic domains. Successively, the information on the reciprocal domain orientation stored in the .p4p file was used to integrate the dataset considering the simultaneous presence of both domains. After that, the resulting intensities set was scaled, corrected for absorption and merged with the help of the *TWINABS* [10] program. As a result, the output in HKLF5 format with a flag indicating the original domains, was generated. Using the latter and testing one more time the charge flipping procedure, the structural model was immediately found and element species were correctly assigned. The Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> was of monoclinic symmetry (space group  $P2_1/m$ , mP34-Tm<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>) and contained 3 Lu, 2 Pd and 6 Ge crystallographic sites. All the atom positions were completely occupied and did not manifest any considerable amount of statistical mixture. The anisotropically refined Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> showed excellent residuals and flat difference Fourier maps (see Table 1). The refined volume ratio of twinned domains was 0.49/0.51.

The *RLATT* program was used to generate a picture showing the distribution of X-ray diffraction spots originating from the two domains, differentiated by color, in Figure 1 (upper part). The distribution of the non-overlapped peaks of the second domain was also easily visible on the precession photo of the *h3l* zone, demonstrated in Figure 1 (lower part). In the same figure, a schematic real space representation of the mutual orientation of the twinned-crystal components is shown.



precession photo of h3l zone

**Figure 1.** Twin law and reciprocal orientation of the two domains in the  $Lu_5Pd_4Ge_8$  twinned crystal (**left**); distribution of the diffraction peaks in the reciprocal space (**right**). Nodes of the reciprocal pattern for each domain are shown in white and green, and overlapped peaks are yellow. On the experimental precession photos of the *h3l* zone, arrows indicate the directions along which the second domain peaks are easily visible.

Indexing of the diffraction dataset of the Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> single crystal gave an orthorhombic base centered unit cell with a = 4.137, b = 6.919, c = 13.823 Å. Systematic extinction conditions related to the presence of symmetry elements were not found for this dataset. The structure solution was found in *Immm* with the aid of the charge flipping algorithm implemented in *JANA2006* [27]. The proposed preliminary structural model contained five crystallographic sites, giving the Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> formula and corresponding to the *oI22*-Gd<sub>3</sub>Cu<sub>4</sub>Ge<sub>4</sub> prototype. Partial site occupation (due to a possible statistical mixture of the species) was checked in separate cycles of least-squares refinement, but no significant deviation from full occupation was detected. The final structure model was refined as stoichiometric with the anisotropic displacement parameters for all crystallographic sites, giving small residual factors and a flat difference Fourier map (see Table 1). The standardized atomic coordinates for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> are given in Table 3.

Atom	Site	x/a	y/b	z/c	U <sub>eq</sub> (Å <sup>2</sup> )				
Lu <sub>5</sub> Pd <sub>4</sub> Ge <sub>8</sub>									
Lu1	2 <i>e</i>	0.71858(8)	1/4	0.93028(6)	0.0047(1)				
Lu2	4f	0.13606(7)	0.11370(2)	0.78913(7)	0.0051(1)				
Lu3	4f	0.62176(8)	0.11902(2)	0.28943(7)	0.0056(1)				
Pd1	4f	0.07436(13)	0.08476(3)	0.14089(12)	0.0072(1)				
Pd2	4f	0.42601(13)	0.58211(3)	0.35985(12)	0.0075(1)				
Ge1	2e	0.0515(2)	1/4	0.28977(15)	0.0081(2)				
Ge2	2 <i>e</i>	0.3343(2)	1/4	0.58221(15)	0.0078(2)				
Ge3	2 <i>e</i>	0.7797(2)	1/4	0.5814(2)	0.0063(2)				
Ge4	4f	0.15453(17)	0.04252(5)	0.44776(16)	0.0071(1)				
Ge5	2e	0.2797(2)	1/4	0.0606(2)	0.0048(2)				
Ge6	4f	0.34622(17)	0.54443(4)	0.05049(16)	0.0060(1)				
			Lu <sub>3</sub> Pd <sub>4</sub> Ge <sub>4</sub>						
Lu1	2 <i>a</i>	0	0	0	0.0110(2)				
Lu2	4j	1/2	0	0.37347(4)	0.0081(2)				
Pd	81	0	0.30094(10)	0.32738(5)	0.0155(3)				
Ge1	4h	0	0.18745(17)	1/2	0.0084(3)				
Ge2	4i	0	0	0.21754(10)	0.0132(3)				

**Table 3.** Atomic coordinates standardized by Structure Tidy [30] and equivalent isotropic displacement parameters for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>.

Similar to  $(Tm/Er)_5Pd_4Ge_8$  [4], the presence of Ge covalent fragments in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> was obvious. Among these, there were two almost identical Ge–Ge dumbbells distanced at 2.49 Å and one more finite fragment composed of four germanium atoms having a *cis*-configuration (Figure 2, Table 4). The latter manifests a small geometrical distortion from the ideal conformation due to slightly different chemical arrangements around terminal Ge atoms (terminal atoms are located at 2.56 and 2.63 Å far from central dumbbell; the internal obtuse angles are ca. 111° and 113°, respectively). The *cis* unit is planar and lays at the mirror plane of the  $P2_1/m$  space group. The cited covalent fragments are joined together through Pd–Ge contacts shortened with respect to metallic radii sum (ranging from 2.51 to 2.73 Å) in a complex network hosting Lu atoms in the biggest cavities (see Figure 2). The shortest Lu–Pd and Lu–Ge contacts do not manifest noticeable deviations from the expected values and are ca. 3.0 Å.

Central Atom	Adjacent Atoms	d (Å)	-iCOHP	Central Atom	Adjacent Atoms	d (Å)	-iCOHP	Central Atom	Adjacent Atoms	d (Å)	-iCOHP
Lu1	Ge6 (×2)	2.853	1.26	Lu3	Ge5	2.904	1.25	(1 <i>b</i> )Ge6	Ge6	2.494	2.39
	Ge1	3.025	0.81		Ge3	2.938	1.25		Pd1	2.516	2.16
	Ge5	3.033	1.02		Pd1	3.042	0.71		Pd2	2.533	2.12
	Ge3	3.036	0.85		Ge1	3.051	0.92		Pd1	2.619	1.80
	Ge2	3.064	0.79		Pd2	3.063	0.68		Lu1	2.853	1.26
	Ge5	3.069	0.81		Ge6	3.072	0.90		Lu2	3.016	0.96
	Pd1 (×2)	3.194	0.52		Ge6	3.094	0.75		Lu2	3.050	0.80
	Pd2 (×2)	3.258	0.46		Pd2	3.100	0.63		Lu3	3.072	0.90
Lu2	Ge5	2.857	1.29		Ge4	3.105	0.71		Lu3	3.094	0.75
	Ge3	2.918	1.20		Ge4	3.120	0.84	Pd1	Ge6	2.516	2.16
	Ge2	2.994	0.99		Pd1	3.236	0.52		Ge4	2.526	2.11
	Ge6	3.016	0.95		Ge4	3.493	0.27		Ge1	2.606	1.66
	Ge4	3.043	0.91	(1 <i>b</i> )Ge3	Ge2	2.559	1.92		Ge6	2.619	1.80
	Ge4	3.043	0.79		Pd2 (×2)	2.699	1.46		Ge5	2.730	1.35
	Ge6	3.050	0.80		Lu2 (×2)	2.918	1.20		Lu3	3.042	0.71
	Pd1	3.087	0.68		Lu3 (×2)	2.938	1.25		Lu2	3.087	0.68
	Pd1	3.104	0.63		Lu1	3.036	0.86		Lu2	3.104	0.63
	Pd2	3.114	0.64	(1 <i>b</i> )Ge4	Ge4	2.492	2.48		Lu1	3.194	0.52
	Pd2	3.156	0.57		Pd2	2.512	2.14	Pd2	Ge4	2.512	2.14
(2b)Ge1	Ge2	2.484	2.98		Pd1	2.526	2.11		Ge6	2.533	2.12
	Pd1 (×2)	2.606	1.66		Pd2	2.566	1.94		Ge4	2.566	1.94
	Ge5	2.627	1.69		Lu2	3.043	0.91		Ge2	2.649	1.53
	Lu1	3.025	0.81		Lu2	3.043	0.79		Ge3	2.699	1.46
	Lu3 (×2)	3.051	0.92		Lu3	3.105	0.71		Lu3	3.063	0.68
(2b)Ge2	Ge1	2.484	2.98	(1 <i>b</i> )Ge5	Ge1	2.627	1.69		Lu3	3.100	0.63
	Ge3	2.559	1.92		Pd1 (×2)	2.730	1.35		Lu2	3.114	0.65
	Pd2 (×2)	2.649	1.53		Lu2 (×2)	2.857	1.29		Lu2	3.156	0.58
	Lu2 (×2)	2.994	1.00		Lu3 (×2)	2.904	1.26				
	Lu1	3.064	0.79		Lu1	3.033	1.02				
					Lu1	3.069	0.81				

**Table 4.** Interatomic distances and integrated crystal orbital Hamilton populations (-*i*COHP, eV/cell) at  $E_F$  for the strongest contacts within the first coordination spheres in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>. Symbols (2*b*) and (1*b*) indicate the number of homocontacts for corresponding Ge species. For more details on this, see next paragraph.

The Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> contains less germanium with respect to Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and, consequently, only a simple Ge–Ge dumbbell forms being, however, more stretched (2.59 Å, Table 5). The trend of other interactions is similar as for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>; Pd and Ge construct an extended network with infinite channels of hexagonal and pentagonal forms hosting Lu atoms.



**Figure 2.** Crystal structures of Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>. The Pd–Ge frameworks are evidenced by dotted lines. Ge–Ge covalent bonds are shown by red sticks. Selected fragments, discussed in the text, are pictured at the bottom. Selected interatomic distances (Å) are indicated. ThCr<sub>2</sub>Si<sub>2</sub>-like fragments are evidenced in blue.

**Table 5.** Interatomic distances and integrated crystal orbital Hamilton populations (-*i*COHP, eV/cell) at  $E_F$  for the strongest contacts within the first coordination spheres in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>. Symbols (1*b*) and (0*b*) indicate the number of homocontacts for corresponding Ge species. For more details on this, see the next paragraph.

Central Atom	Adjacent Atoms	d (Å)	-iCOHP	Central Atom	Adjacent Atoms	d (Å)	-iCOHP
Lu1	Ge4 (×4)	2.992	1.21	(0b)Ge2	Pd (×4)	2.562	1.88
	Ge5 (×2)	3.006	1.05		Pd (×2)	2.577	1.86
	Pd (×8)	3.445	0.41		Lu2 (×2)	2.988	0.83
Lu2	Ge5 (×2)	2.988	0.83		Lu1	3.006	1.05
	Ge4 (×4)	3.003	0.99	Pd	Ge4	2.512	2.23
	Pd (×4)	3.003	0.79		Ge5 (×2)	2.562	1.88
	Pd (×2)	3.100	0.58		Pd	2.755	0.97
(1 <i>b</i> )Ge1	Pd (×2)	2.512	2.23		Lu2 (×2)	3.003	0.79
	Ge1	2.595	1.82		Pd (×2)	3.058	0.46
	Lu1 (×2)	2.992	1.22		Lu2	3.100	0.58
	Lu2 (×4)	3.003	0.99		Lu1 (×2)	3.445	0.41

One more structural relation can be proposed for the title compounds: both compounds contain common structural  $ThCr_2Si_2$ -like building blocks [31] (highlighted by blue lines in Figure 2) defined in many related compounds as "linkers" within various polyanionic fragments [32].

#### 3.2.2. Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>: Structural Relationships

Looking for structural relationships is not an easy task, since this process is often strongly affected by human factors and is based on sometimes arbitrary criteria. From this point of view, one of the most rigorous approaches is based on the symmetry principle within the group-subgroup theory [33]. The most frequent chemical reason causing the reduction of symmetry is so-called "coloring", which can be interpreted as an ordered distribution of different chemical elements within distinct Wyckoff sites. Müller [34] and Pöttgen [35] depict numerous examples of these.

Structural relationships between  $Tm_5Pd_4Ge_8$  (isostructural with  $Lu_5Pd_4Ge_8$ ) and  $RE_3T_2Ge_3$  (T = late transitional element) were proposed in the literature [2] based on topological similarities between polyanionic fragments and the spatial distribution of cations. An alternative description of relationships between the abovementioned structures in terms of symmetry reduction is proposed here. The stoichiometries of these compounds are related as follows:

$$4 R E_3 T_2 G e_3 - 2 R E + 4 G e = 2 R E_5 T_4 G e_8$$
(1)

This relation, even if purely numerical, finds support when comparing the crystal structures of the two chemically affine representatives  $Lu_3Fe_2Ge_3$  (*oS32*) and  $Lu_5Pd_4Ge_8$  (*mP34*). As is evidenced in Figure 3, one of the Lu sites in the former is substituted by a Ge dumbbell in the latter.



**Figure 3.** Structural similarities between  $Lu_3Fe_2Ge_3$  and  $Lu_5Pd_4Ge_8$ . The polyanionic networks are shown by dotted lines, and covalent Ge fragments are joined by red sticks. The grey rectangle evidences regions of the crystal space where  $Lu/Ge_2$  substitution takes place (for details see text).

From the chemical interaction point of view, this should be a drastic change; instead, the remaining atoms apparently do not suffer noticeable displacements. This is why it was checked whether a Bärnighausen tree might be constructed relating the *oS32* and *mP34* models. In fact, only two reduction steps were needed:

- a *traslationengleiche* (t2) decentering leading to a monoclinic Niggli cell (*mP16-P2*<sub>1</sub>/*m*).
- a *klassengleiche* transformation (k2) giving a monoclinic model with doubled cell volume  $(mP32-P2_1/m)$ . As a result, all the independent sites split in two (see Figure 4).

The Lu2' site (2*e*: 0.211 1/4 0.430) was further substituted by two germanium atoms (positions Ge1 and Ge2 in the final *mP*34-*P*2<sub>1</sub>/*m* structural model). As a result, the already cited *cis*-Ge4 unit forms (see Figure 2), whose chemical role is discussed in the next section. The presence of the *cis*-Ge<sub>4</sub> units is quite intriguing, since the *trans* conformation is more favorable in numerous molecular chemistry examples. Therefore, it was decided to generate a structural model of Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> composition hosting the *trans*-Ge unit and optimize it (see Figure S1 and Table S1). The relaxed structure perfectly coincided with the experimental results, confirming that minimal energy is associated with the *cis* conformation. More details on this, including an animation showing the evolution of the structural model after each relaxation step, are available in the Supplementary Material.



**Figure 4.** Evolution of the atomic parameters within the Bärnighausen formalism accompanying the symmetry reduction from  $Lu_3Fe_2Ge_3$  to  $Lu_5Pd_4Ge_8$  structures. The background colors correspond to the atom markers in the figures through the text.

## 3.3. Chemical Bonding Analysis

Frequently, chemical bonding in polar intermetallics is preliminary addressed using the *Zintl-Klemm* concept. Taking into account the interatomic distances between Ge atoms, the presence of  $[(1b)Ge^{3-}]$  with  $[(2b)Ge^{2-}]$  Zintl species in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and  $[(1b)Ge^{3-}]$  with  $[(0b)Ge^{4-}]$  ones in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> could be guessed. In order to guarantee the precise electron count, the average number of valence electrons per Ge atom [*VEC*(Ge)] should amount to 6.75 for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and to 7.50 for Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>. Although it is reasonable to hypothesize a formal charge transfer of 3 valence electrons per Lu atom (Lu<sup>3+</sup>), as a first approximation, the Pd could be considered as a divalent cation (Pd<sup>2+</sup>) or a neutral species (Pd<sup>0</sup>). However, none of the possible electron distribution formulae listed below are suitable for the studied compounds, giving *VEC*(Ge) values that deviate somewhat from ideal.

 $Lu_5Pd_4Ge_8 (Pd^0) \quad VEC(Ge) = 5.875$  $Lu_5Pd_4Ge_8 (Pd^{2+}) \quad VEC(Ge) = 6.875$  $Lu_3Pd_4Ge_4 (Pd^0) \quad VEC(Ge) = 6.250$  $Lu_3Pd_4Ge_4 (Pd^{2+}) \quad VEC(Ge) = 8.250$ 

Even if the obtained VEC(Ge) values are closer to 6.75/7.50, in the case of  $Pd^{2+}$ , this assumption is not coherent with the valence electrons flow when considering any of the known electronegativity

scales. For example, taking into account the *Pearson* electronegativity values for Pd (4.45 eV) and Ge (4.60 eV) it is clear that a charge transfer from Pd to Ge is hardly probable. Strictly speaking, it is not possible to successfully apply the (8–*N*) rule to interpret the Ge–Ge covalent interactions. Thus, it becomes clear that these simplified considerations are not sufficient to account for the chemical bonding of the studied intermetallics. In particular, it is not reliable to consider covalent Ge fragments as isolated and more complex interactions should be taken into account. Therefore, a deeper chemical bonding investigation was conducted.

In Table 6, the volumes of the atomic basins and Bader effective charges for all the atoms in  $Lu_5Pd_4Ge_8$  and  $Lu_3Pd_4Ge_4$  are listed together with those for the same species in their pure element form. Comparing these values, one can qualitatively estimate the chemical role of constituents in binary/ternary compounds.

Element/Compound	Atom/Site	Volume, [Å <sup>3</sup> ]	QTAIM Charge, Q <sup>eff</sup>	Compound	Atom/Site	Volume, [Å <sup>3</sup> ]	QTAIM Charge, Q <sup>eff</sup>
Lu ( <i>hP</i> 2)	Lu/2c	29.74 #	0	Lu5Pd4Ge8	Lu1/2e	15.88	+1.45
Pd ( <i>cF</i> 4)	Pd/4a	14.71 #	0	(mP34)	Lu2/4f	15.48	+1.48
Ge (cF8)	Ge/8a	22.66 #	0		Lu3/4f	15.85	+1.51
					Pd1/4f	19.91	-0.79
$Lu_3Pd_4Ge_4$	Lu1/2a	16.90	+1.57		Pd2/4f	19.77	-0.76
(oI22)	Lu2/4j	15.05	+1.53		(2b)Ge1/2e	19.39	-0.23
	Pd/8l	19.43	-0.67		(2b)Ge2/2e	19.51	-0.30
	(1b)Ge1/4h	22.35	-0.89		(1 <i>b</i> )Ge3/2e	22.66	-0.87
	(0b)Ge2/4i	16.42	-0.09		(1b)Ge4/4f	18.73	-0.30
					(1 <i>b</i> )Ge5/2 <i>e</i>	23.96	-1.14
					(1 <i>b</i> )Ge6/4 <i>f</i>	19.67	-0.59

**Table 6.** Calculated QTAIM effective charges and atomic basin volumes for Lu, Pd and Ge in their elemental structure, in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>.

<sup>#</sup>—the QTAIM volumes of atoms in pure elements are equal to the volumes of their Wigner–Seitz polyhedra; structural data were taken from Ref [1].

In both ternary germanides, the QTAIM basins of Lu were shrunk with respect to Lu-hP2, and the corresponding charges oscillated around +1.5, confirming the active metal-like role of Lu. The significant difference between Lu effective charges and the formal charges suggest that some of its valence electrons may contribute to covalent interactions.

The palladium atoms had similar volumes of atomic basins (ca. 20 Å<sup>3</sup>) and were negatively charged ( $-0.7 \div -0.8$ ), suggesting a bonding scenario coherent with the electronegativity values, i.e., with Pd taking part in a polyanionic network, as was hypothesized from the crystal structure analysis.

It is noteworthy that in the same compound, Ge atoms had pronounced differences in charge values (always negative) from site to site. More on the structural/chemical reasons for this will be discussed in the following.

The total and projected DOS for Lu, Pd and Ge for the studied intermetallics are shown in Figure 5. Orbital projected DOS can be found in the Supplementary Material (Figure S3). Focusing on the total DOS, a difference between the two compounds at the Fermi energy ( $E_F$ ) is evident: for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> a pseudo-gap is visible just above  $E_F$ , instead for Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> the Fermi level corresponds to a local maximum of the DOS, indicating a potential electronic instability. This might be a sign of particular physical properties (e.g., superconductivity or magnetic ordering) [36] or of small structural adjustments (e.g., off-stoichiometry due to statistical mixture or increase of vacancy concentration) [37] which, adequately modelled, would shift the  $E_F$  towards a local minimum. Even if EDXS elementary composition is compatible with a slightly off-stoichiometry, there is no strong indication of this coming from XRD data, so, the stoichiometric model was considered here. Further experimental investigations will be carried out aiming physical properties studies of this compound.



Figure 5. Total and projected DOS for the two studied compounds.

For both compounds, the valence orbital mixing of the three components over the whole energy range is noteworthy. Below  $E_F$ , both DOSs showed a gap of around -7 eV separating the two regions, with the lowest being mostly dominated by the 4s Ge states. The Pd-d states are mainly distributed in the range between -5 and -2.5 eV. Their width and energy overlapped with 4p Ge and Lu states, supporting the bonding relevance of Pd–Ge and Pd–Lu interactions. The fact that the majority of Pd 4d states are located well below the  $E_F$  indicates the electron acceptor character of this species. A significant contribution of 5d Lu states just below the  $E_F$  is a common feature of cations in polar intermetallics, characterized by an incomplete charge transfer (confirmed here also by Bader charge values).

Although the *Zintl–Klemm* (8–*N*) rule cannot be applied for the title compounds, it was decided to trace interaction similarities comparing the electronic structures of ideal Zintl anions  $\text{Ge}_2^{6-}$  and *cis*- $\text{Ge}_4^{10-}$  coming from the extended Hückel calculation with those obtained by means of TB-LMTO-ASA, in terms of COHP curves. Molecular orbital diagrams (MO) for  $\text{Ge}_2^{6-}$  (point group  $D_{\infty h}$ ) and  $\text{Ge}_4^{10-}$  (the point symmetry of this anion was forced to  $C_{2v}$  fixing for all distances to 2.56 Å and obtuse internal angles to 111°) are presented in the Supplementary Materials (Figure S2) with the accordingly labeled orbitals.

In Figure 6a, the molecular orbital overlap population (MOOP) for  $\text{Ge}_2^{6-}$  is shown, together with COHP curves for Ge–Ge interactions (in dumbbells) existing in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> and Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>.

These partitioning methods could not be directly compared, since MOOP partitions the electron number, instead, COHP partitions the band structure energy. Since they both permit to easily distinguish between bonding and antibonding states, it was decided to perform a qualitative comparison targeting to figure out the similarities/differences between the isolated molecular fragments analogous with those found in the studied compounds.

The presence of the gap (at ca. -7eV) may be attributed to the energy separation of the  $\sigma ss$  and  $\sigma^*ss$  of Ge<sub>2</sub> dumbbells from the  $\sigma p$ ,  $\pi p$  and  $\pi^*$  orbitals. For the Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> there are some occupied  $\pi^*$  states close to E<sub>F</sub>, whereas in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>, the cited interactions are almost optimized at E<sub>F</sub>. From these observations it derives that Ge dumbbells are not completely polarized; for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> the dispersion of  $\sigma$  and  $\sigma^*$  states is more pronounced. One of the possible explanation of this is the existence of additional covalent interactions between germanium dumbbells and neighboring atoms.



**Figure 6.** Extended Hückel calculated Molecular Orbital Overlap Population (MOOP) plot for the Ge<sub>2</sub><sup>6–</sup> (**a**) and *cis*-Ge<sub>4</sub><sup>10–</sup> (**b**) anions together with the corresponding Crystal Orbital Hamilton Population (COHP) for Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> and Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> (**I** and **II** corresponds to two distinct dumbbells). The degeneracy of the  $\pi$  levels for Ge<sub>2</sub><sup>6–</sup> is removed for the sake of clarity. The HOMO energy is set in correspondence to E<sub>F</sub>.

From the structural data it is known that in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>, Ge atoms are distanced at 2.59 Å as in diverse metal-like salts studied before [38–40]. Instead, in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> this distance is shortened to 2.49 Å. Usually, the trend of Ge–Ge dumbbell distances is related with electrostatic repulsion between atoms. This statement is coherent with integrated COHP values (*–i*COHP, see Tables 4–6), reflect the same trend, being of -1.82 eV/cell for Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> and of -2.39 and -2.48 eV/cell for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>.

Within the *cis*-Ge<sub>4</sub><sup>10–</sup> anion the number of covalent interactions is higher, as a result the energy dispersion of its molecular states increases. For example, in the range  $-18 \div -14$ eV there are four MOs instead of two MOs for dumbbells. A very similar trend/type of interactions derives from COHP curves for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>. As for the dumbbells, the interactions for the *cis* fragment are optimized at the E<sub>F</sub> confirming its partial polarization.

Based on -iCOHP values listed in Tables 4–6 it derives that Pd–Ge interactions are very relevant, so one may assume the covalent type of bonding between them. The –COHP plots in Figure 7 confirm that they are mainly of bonding type over a large range below  $E_F$  with a weak unfavorable antibonding interaction in the vicinity of  $E_F$ , probably due to electrostatic repulsion between Ge orbitals and filled *d* states of Pd.

Inside Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> the presence of a Pd–Pd short interaction can be highlighted. The –COHP plots for this are similar to those reported for Ca<sub>2</sub>Pd<sub>3</sub>Ge [41] showing a sharp antibonding character around -3 eV commonly attributed to enhanced repulsion between filled *d* states of Pd. Nevertheless, they are of bonding type in average as deducible from the –*i*COHP values for this interaction (0.97 eV/cell), comparable to those reported in [41].

The remaining Lu–Pd and Ge–Lu interactions are weaker being however very similar for both germanides. All of them are of bonding type, Lu–Pd interactions are practically optimized at Fermi level. Numerous interactions between Lu and Pd (Lu and Ge) suggest that some covalent-like interaction may exist due to mixing between *d* states of Lu and Pd (or *d* states of Lu with *p* of Ge; similarly, as it was reported for Ca<sub>5</sub>Ge<sub>3</sub> [36] and CaSi [42]). More detailed studies are needed in order to interpret these interactions.

The existence of the complex Pd–Ge polyanion and the electronegativity difference between Pd and Ge explains the trend of Ge species charges (see Tables 4 and 5, and Figure 2). The Ge dumbbell in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> has four neighboring Pd atoms, instead those in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> install six Pd–Ge polar interactions. As a result, the latter Ge species has lower negative charges. The same is true for isolated Ge atoms with six palladium atoms around in Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub>: its charge approaches to zero. Within crystal structure, the number of Pd–Ge contacts is the same for terminal and central atoms of *cis*–Ge<sub>4</sub> units; thus, their charges trend is similar as for ideal *cis*-Ge<sub>4</sub><sup>10–</sup> anion, terminal atoms being more negative.



Figure 7. Crystal Orbital Hamilton Populations (-COHP) for selected interactions for the two studied compounds.

# 4. Conclusions

The two new Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> polar intermetallics were synthesized and characterized in this work. They were found to crystallize in the *mP*34–Tm<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and *ol*22–Gd<sub>3</sub>Cu<sub>4</sub>Ge<sub>4</sub> structures respectively. A detailed description of crystal structure solution in the case of the non-merohedral twinned crystal of Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> was proposed, highlighting the difficulties/problems encountered here along with practical suggestions to manage them.

Joined crystal chemical analysis and combined DFT studies suggest the presence of [Pd<sub>4</sub>Ge<sub>8</sub>]<sup>7.4–</sup> and [Pd<sub>4</sub>Ge<sub>4</sub>]<sup>4.6–</sup> polyanions. The interactions of Lu with these frameworks cannot be viewed as purely ionic as derives from its states distribution, COHP analysis and Bader charges. The Lu–Pd and Lu–Ge bonding interactions are one of the most interesting aspects arisen from our study and their nature deserves further investigations.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4352/8/5/205/s1, Figure S1: Schematic representation of the structural relationships between "cis" and "trans" Ge<sub>4</sub> fragments in Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> models; Figure S2: Molecular orbitals diagram for Ge<sub>2</sub><sup>6–</sup> (a) and *cis*-Ge<sub>4</sub><sup>10–</sup> (b) as generated by CACAO; Figure S3: Total DOS for Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> and Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> together with the orbital projected DOS for each species; Table S1: Atomic parameters for "trans"-Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> model. Video S1: Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub>\_trans-cis\_optimization, Lu<sub>5</sub>Pd<sub>4</sub>Ge<sub>8</sub> CIF file, Lu<sub>3</sub>Pd<sub>4</sub>Ge<sub>4</sub> CIF file.

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