



Article Hybrid-Density Functional Calculations of Structural, Electronic, Magnetic, and Thermodynamic Properties of α -Cu₂P₂O₇

Xiaoyong Yang ^{1,2}, Ping Zhang ³ and Pavel Korzhavyi ^{1,*}

- ¹ Department of Materials Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
- ² State Key Laboratory of Environment-Friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, China
- ³ Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
- * Correspondence: pavelk@kth.se; Tel.: +46-8-790-9193

Abstract: We present a comparative study (using PBE, PBE0, and HSE functionals) of electronic and atomic structure, magnetism, and phonon dispersion relations of α -Cu₂P₂O₇. Four possible magnetic configurations are considered, FM, AFM-1, AFM-2, and AFM-3. The calculations reveal that α -Cu₂P₂O₇ is mechanically and thermodynamically stable. The elastic moduli indicate a weak resistance of the compound to volume and shear deformations. The electronic structure at the valence band maximum is dominated by O, with a small admixture of Cu- $d_{x^2-y^2}$ states. The conduction band results from the hybridization between Cu and O states which, in the case of AFM-2, produces the largest band gap of 3.966 eV and the smallest magnetic moment of $\pm 0.785 \ \mu_B$ on Cu. AFM-2 is found to be the lowest-energy structure that may be viewed as consisting of quasi-one-dimensional $-Cu_1-Cu_2-Cu_3-Cu_4-$ chains along the *b* axis; the antiferromagnetism is due to two identical Cu-O-Cu paths with a bond angle of 100.301°. The phonon spectra exhibit four distinct frequency ranges corresponding to different vibrational modes of ions and ionic groups. Thus, a quantitative description of the structural, electronic, and magnetic properties of α -Cu₂P₂O₇ is possible using the HSE hybrid functional, which enables computational studies of transition metal pyro compounds.

Keywords: copper pyrophosphate; hybrid-functional calculations; elastic properties; electronic structure; antiferromagnetism; phonon dispersion relations

1. Introduction

Transition metal pyro compounds $M_2X_2O_7$ with M-cations (M = Cr, Mn, Fe, Ni, Co, Cu, Zn, Cd, Mg, Hg) and X = P, As, Se, Ge have been widely used in catalysts [1,2], supercapacitors [3–6], photoluminescence devices [7], and some other applications [8–10] due to their excellent chemical stability, facile preparation, magnetic properties, and non-toxicity [11–13]. The $M_2X_2O_7$ compounds are observed in two types of structure, i.e., dichromate structure type and thortveitite structure type, depending on the ratio of the M to X ionic radii. Amongst these, copper pyrophosphate (Cu₂P₂O₇) has been well characterized and received much attention as a prospective material for advanced energy storage devices, lightning, photovoltaic devices, sensors, catalysts, etc. [2–7,10].

The room-temperature α phase of Cu₂P₂O₇ with space group C2/*c* undergoes a solidsolid phase transition to β -phase with space group C2/*m* at a slightly elevated temperature of about 339–383 K, as has been established by X-ray diffraction (XRD) [14]. The structure is composed of pyrophosphate (diphosphate) [P₂O₇]^{4–} ionic groups arranged into layers that are parallel to the (001) lattice plane, and Cu²⁺ cations in irregular octahedral coordination by oxygen atoms. Cu²⁺ octahedra form a pseudo-hexagonal network between the adjacent [P₂O₇]^{4–} layers. Each pyrophosphate unit [P₂O₇]^{4–} consists of two monophosphate



Citation: Yang, X.; Zhang, P.; Korzhavyi, P. Hybrid-Density Functional Calculations of Structural, Electronic, Magnetic, and Thermodynamic Properties of α -Cu₂P₂O₇. *Appl. Sci.* **2023**, *13*, 498. https://doi.org/10.3390/app13010498

Academic Editors: Leonid Burakovsky and Alexander I. Landa

Received: 3 November 2022 Revised: 20 December 2022 Accepted: 24 December 2022 Published: 30 December 2022



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). tetrahedra $[PO_4]^{3-}$ which share one corner via the bridging O(1) atom. In the α phase, the P–O(1)–P bond angle is 157°, whereas it is 180° in the β phase [15]. Robertson and Calvo reported that the β phase could be described simply as a disordered α phase of Cu₂P₂O₇, which manifests interesting thermal and dielectric properties [15]. Additionally, the β phase exhibits twice as small *c* lattice parameter and a disordered arrangement of the bridging O atoms shared by the two [PO₄] tetrahedra in a pyrophosphate group [16]. Since the α phase is structurally similar to the β phase of Cu₂P₂O₇, in the present work we focus on the α phase which is fully ordered and stable at room temperature.

It is well understood that the properties of materials strongly depend on the crystal structure, dimensionality, purity, morphology, and size of their constituent particles [17–20]. Thus, various methods to synthesize $Cu_2P_2O_7$ with controllable microstructure, shape, and particle size have been considered [5,6,13,17,21], such as solid-state routes, sol-gel synthesis, chemical bath deposition, co-precipitation, successive ionic layer and adsorption reaction strategy, carbothermal reduction method, and a simple hydrothermal method. Correspondingly, the physical and chemical properties of $Cu_2P_2O_7$ such as structural, morphological, optical, magnetic, and electrochemical properties, thermodynamic stability and phase transitions have been investigated experimentally and theoretically [6,12,13,16,17,22,23].

The magnetic behavior of α -Cu₂P₂O₇ was studied in the early 1970s. Tentative models of the magnetic structure were derived from neutron diffraction and nuclear magnetic resonance data; an antiferromagnetic (AFM) ordering was reported at 27 K [24,25]. Theoretically, the AFM order in α -Cu₂P₂O₇ was confirmed by Janson et al., in which the magnetism was found to originate from the half-filled Cu $3d_{x^2-y^2}$ orbital states [12]. The interlayer Cu–Cu coupling is relatively weak and short-ranged since it is mediated by a thick pyrophosphate [P₂O₇]^{4–} layer composed of [PO₄] tetrahedral units. Moreover, based on a comparison of α -Cu₂P₂O₇ and α -Cu₂As₂O₇ with β -Cu₂V₂O₇, Janson et al. found that *p* cations of P and As atoms donate electrons to the neighboring O anions, leading to more ionic P–O bonds, which confines the interlayer superexchange to the Cu–O–Cu path [12]. However, the electronic band structure calculations employing local density approximation (LDA) wrongly predict a metallic ground state [12], implying that strong electron correlations in Cu 3*d* states, included in that work via Hubbard-*U* corrections (LDA+*U*), are critical for obtaining microscopic insight into the electronic and magnetic properties of complex compounds.

Previous studies concluded that generalized gradient approximation (GGA) combined with the Hubbard-*U* correction (GGA+*U*) gives correct results for the electronic and magnetic properties of Cu₂V₂O₇ [23,26]. Thus, the calculations yielded band gap values of 2.85 eV [26] and 3.17 eV [23] and magnetic moments on Cu atoms of 0.84 μ_B [26] and 0.8 μ_B [23] in the AFM order, which is compatible with experimental findings [12,23]. Moreover, a negative thermal expansion behavior of α -Cu₂P₂O₇ was disclosed recently by the X-ray and neutron diffraction investigations, which is caused by the transverse vibrations of O atoms [13]. Although the Raman spectra of Cu₂P₂O₇ in α and β phases have been studied experimentally [16] and also theoretically including the full phonon dispersion relations [23], the whole set of elastic, electronic, and magnetic properties of Cu₂P₂O₇ have not been systematically studied.

Motivated by the studies mentioned above, here we systematically study the atomic, electronic, and magnetic structure, as well as the elastic properties and lattice dynamics, of α -Cu₂P₂O₇ using hybrid-functional calculations based on density functional theory (DFT). Importantly, we find that PBE0 and HSE hybrid functionals give more accurate descriptions of the electronic structure and thermodynamic properties of α -Cu₂P₂O₇ relative to the accuracy of semi-local PBE functional calculations, thus demonstrating the usefulness of the hybrid-functional approach in studies of transition metal pyro compounds. The remainder of this article is organized as follows. The first-principles calculation methods are briefly described in Section 2.1. Section 2.2 presents the details of the elastic constant calculations. In Section 3 we report and discuss the crystal structure, thermodynamic

stability, and other properties derived from the calculated electronic and phonon spectra. Finally, the conclusions are drawn in Section 4.

2. Methodology

2.1. Computational Details

In this work, density functional theory (DFT) [27] based calculations for α -Cu₂P₂O₇ have been performed using the projector-augmented-wave (PAW) type pseudopotentials with the *Vienna Ab initio Simulation Package* (VASP) code [28,29]. Four possible magnetic configurations are considered, FM, AFM-1, AFM-2, and AFM-3, see Figure 1. Three different approximations to treat the exchange and correlation contributions have been applied: (i) the PBE approach utilizing a standard generalized gradient approximation scheme [30], (ii) the hybrid PEB0 approach [31,32] and (iii) the hybrid HSE method [33,34] as implemented in VASP. In the PBE0 functional, 25% of PBE exchange has been replaced by the exact non-local exchange showing the normal 1/r kernel. When the degree of exact exchange α is allowed to vary, $E_{\chi}^{PBE0}(\alpha) = \alpha E_{\chi}^{exact} + (1 - \alpha) E_{\chi}^{PBE}$; such a case is referred to as the generalized class of functionals [31,32]. Both PBE0 and HSE functionals used in this work mix 25% of the exact Hartree-Fock (HF) exchange with 75% of the PBE exchange functional in their short-range part. However, in the HSE functional, the long-range part of the exact exchange is smoothly replaced with the local expression of the PBE exchange.



Figure 1. Optimized crystal structures for four collinear configurations of magnetic moments on Cu atoms in *α*-Cu₂P₂O₇, one ferromagnetic (FM) and three antiferromagnetic (AFM). (**a**) FM; (**b**) AFM-1; (**c**) AFM-2; (**d**) AFM-3. Large blue, grey, and red balls denote copper, phosphorus, and oxygen atoms, respectively.

The valence basis set included 3*d* and 4*s* states on Cu, 3*s* and 3*p* states on P, and 2*s* and 2*p* states on O. A cutoff energy of 520 eV was chosen for the plane-wave basis set. For each considered functional and magnetic configuration, full structural optimization was performed including the shape and volume of the unit cell. Internal atomic positions were fully relaxed until the Hellmann-Feynman forces on them were less than 0.01 eV/Å. A $3 \times 3 \times 3$ Monkhorst-Pack *k*-point mesh [35] was used to integrate over the Brillouin zone (BZ) for each configuration of α -Cu₂P₂O₇, whose unit cell contained 22 atoms. A dense $5 \times 5 \times 3$ *k*-point mesh was selected to compute the density of states (DOS) and the charge density distributions. Spin polarization was turned on in all the calculations. To have a quantitative description of the charge distribution and transfer, the Bader charge analysis was employed [36]. Phonon frequencies were calculated based on the density functional perturbation theory (DFPT) as implemented in the VASP and PHONOPY [37] packages for the lowest-energy AFM-2 configuration using PBE functional at the PBE-optimized volume. In the interpolation of the force constants for the phonon dispersion curve calculations, $3 \times 3 \times 3$ *k*-point mesh in the first BZ was used. Vibrational contributions to

thermodynamic properties such as (free) energy, entropy, and heat capacity were evaluated, as functions of temperature, from the computed phonon dispersion relationships of α -Cu₂P₂O₇ using the methodology detailed in Section 3.5.

The relative chemical stability of α -Cu₂P₂O₇ was calculated according to the definition of formation energy (per formula unit),

$$\Delta E_f = \frac{1}{2} \{ E(Cu_4 P_4 O_{14}) - 4\mu(Cu) - 4\mu(P) - 14\mu(O) \},$$
(1)

where $E(Cu_4P_4O_{14})$ is the total ground-state energy of the primitive cell containing two $Cu_2P_2O_7$ formula units and $\mu(Cu)$, $\mu(P)$ and $\mu(O)$ are the chemical potentials associated with the pure elements in their standard states [38]. Thus a positive formation energy means that energy must be supplied to form the material, while a negative formation energy implies that the formation is energetically favorable and spontaneous.

For the purpose of comparison of DFT functionals, the formation energy is not a very informative indicator because Equation (1) mixes together the energies of substances with very different types of primary chemical bonding (metallic, ionic, and covalent) for which the DFT functionals perform very differently. For instance, semi-local functionals like PBE perform very well for metals, while hybrid functionals describe the bonding in insulators and molecular substances more accurately than in metals [39].

Another approach [40,41] is to compute the cohesive energy, that is the energy needed to form a solid crystal from the free atoms, which may be defined by replacing the chemical potentials μ in Equation (1) with the energies of the corresponding atomic species. Still, such a definition operates the energies of very different systems (namely, a strongly bonded solid versus free atoms), so it also suffers from the transferability errors of DFT functionals that are quite large for atomization energies [42].

Yet another possibility is to consider the energy of a chemical reaction in which $Cu_2P_2O_7$ compound is formed from a basic oxide, CuO, and an acidic oxide, P_2O_5 [22],

$$2CuO + P_2O_5 \rightarrow Cu_2P_2O_7,$$

calculated as follows:

$$\Delta E_f^{ox} = \frac{1}{2} \{ E(Cu_4 P_4 O_{14}) - E(Cu_4 O_4) - \frac{1}{2} E(P_8 O_{20}) \}.$$
⁽²⁾

Here Cu₄O₄ represents the monoclinic unit cell of CuO structure, space group C2/c, containing four formula units (Z = 4) with an antiferromagnetic alignment of magnetic moments on Cu ions. The calculated lattice parameters by PBE functional is a = 4.667 Å, b = 3.419 Å, c = 5.157 Å, $\beta = 99.4767^{\circ}$, which is very well consistent with the experimental findings [43]. P₂O₅ crystallizes in the orthorhombic structure, space group Pnma, whose unit cell contains four formula units. The calculated lattice parameters by PBE functional are a = 9.613 Å, b = 4.941 Å, c = 7.386 Å, and $\alpha = \beta = \gamma = 90^{\circ}$. The optimized crystal structures of CuO and P₂O₅ are shown in Figure S1.

2.2. Elastic Properties

Elastic constants are critical indicators to understand the response of a material to applied macroscopic stress. The tensor of elastic constants C_{ijkl} is defined by the generalized Hooke's law expressing linear relationships between stress tensor components σ_{ij} and strain tensor components ε_{kl} where each of the indices *i*, *j*, *k*, and *l* runs over the Cartesian basis vectors *x*, *y*, and *z*. The elastic tensor is commonly represented as a 6×6 matrix using the following short-hand notations for pairs of indices $\{ij\}$ and $\{kl\}$: $xx \equiv 1$, $yy \equiv 2$, $zz \equiv 3$, $yz \equiv 4$, $xz \equiv 5$, and $xy \equiv 6$. Owing to the structural symmetry, the number of independent non-zero elastic constants decrease from 21 to 13 for the monoclinic system, which is expressed as follows,

$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0\\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0\\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0\\ 0 & 0 & 0 & C_{44} & 0 & C_{46}\\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0\\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{bmatrix},$$
(3)

The strain energy, which is defined as the change in the total energy per unit cell $E(V, \varepsilon_i)$ relative to the ground state energy $E(V_0, 0)$ of the unstrained crystal, may be expanded as a Taylor series in terms the components of the strain tensor ε_i , i = 1, ..., 6

$$E(V,\varepsilon_i) = E(V_0,0) + V_0 \sum_{i}^{6} \sigma_i \varepsilon_i + \frac{V}{2} \sum_{i,j=1}^{6} C_{ij} \varepsilon_i \varepsilon_j + O(\{\varepsilon_i^3\}).$$
(4)

where V_0 is the undistorted unit cell volume. For the monoclinic structure, elastic constants include 13 independent non-zero tensor components, namely C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} , C_{66} , C_{15} , C_{25} , C_{35} and C_{46} [44]. They may be calculated using the following thirteen different strains,

The strain amplitude δ was varied in steps of 0.005 from -0.025 to 0.025. A detailed description of the calculation procedure used here can be found in Refs. [44,45].

3. Results and Discussion

3.1. Magnetic Structure of α -Cu₂P₂O₇

The crystal structure of monoclinic α -Cu₂P₂O₇ with C2/*c* space group includes two layers of pyrophosphate [P₂O₇] groups; the layers are parallel to the (100) plane. The optimized crystal structures for the four magnetic configurations considered in this work are shown in Figure 1 with the local magnetic moments on the four Cu atoms indicated by arrows. The primitive cell parameters for the ferromagnetic (FM) state, as calculated by PBE functional, are $a_p = b_p = 5.485$ Å, c = 9.411 Å, $\alpha_p = \beta_p = 75.725^\circ$, $\gamma_p = 97.330^\circ$, $V_0 = 260.53$ Å³ and Z = 2 (two Cu₂P₂O₇ formula units per primitive cell). The calculated (standardized, Z = 4) unit cell parameters are listed in Table 1 where they are compared with some of the available theoretical and experimental data [14,15,22,23].

We note that a hydrated form of nanocrystalline copper pyrophosphate exists, whose unit cell (incorporating four Cu₂P₂O₇·2H₂O formula units) is bigger than that of the anhydrous form: a = 11.466 Å, b = 10.204 Å, c = 6.123 Å [46]. Naturally, the molecular volume for the hydrated form, $V_0 = 196.054$ Å³ per Cu₂P₂O₇·2H₂O formula unit, is bigger than that for the anhydrous form, $V_0 = 130.265$ Å³ per Cu₂P₂O₇ formula unit, by the volume of two H₂O molecules.

In copper pyrophosphate, only Cu²⁺ ions are calculated to carry local magnetic moments corresponding to spin 1/2. Each Cu²⁺ ion is surrounded by five O atoms forming a [CuO₅] polyhedron with the volume of 6.905 Å³ and Cu–O bond lengths in the range 1.913–2.316 Å. Besides, the shortest Cu–Cu distance (along the crystallographic direction *b*) is calculated to be ~3.12 Å. Importantly, for this Cu–Cu pair there are two identical Cu–O–Cu paths with a bond angle ∠Cu–O–Cu of 101.735°, as shown in Table 2. According to previous studies on the nearest-neighbor (NN) exchange coupling, the closeness of ∠Cu–O–Cu to 90° indicates a sizeable ferromagnetic contribution, based on the Goodenough-Kanamori rules [12,47,48]. Hence, it is natural to expect the superexchange interaction to favor an antiferromagnetic order for the Cu–Cu NN pair, due to the deviation of Cu–O–Cu

bond angle from 90°. The calculated Cu–Cu distance and Cu–O–Cu bond angle is in agreement with the results of previous studies, 3.05–3.33 Å and 100.4–100.8° [12,14,24].

Table 1. Unit cell parameters of α -Cu₂P₂O₇ in comparison with previous theoretical [23] and room-temperature experimental [14,15,22,23] results. Up and down arrows denote a possible order of magnetic moments on sites Cu₁–Cu₄, see Figure 1.

State	Functional	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
FM	PBE	7.245	8.237	9.411	111.922	521.060
$\uparrow\uparrow\uparrow\uparrow$	PBE0	7.072	8.115	9.291	111.003	497.660
	HSE	7.076	8.118	9.299	111.028	498.58
AFM-1	PBE	7.244	8.236	9.405	111.907	520.52
$\downarrow\downarrow\uparrow\uparrow\uparrow$	PBE0	7.066	8.112	9.251	110.914	495.36
	HSE	7.068	8.121	9.256	110.910	496.34
AFM-2	PBE	7.246	8.231	9.405	111.925	520.440
$\downarrow\uparrow\uparrow\downarrow$	PBE0	7.063	8.112	9.252	110.876	495.260
	HSE	7.073	8.116	9.262	110.976	496.48
AFM-3	PBE	7.232	8.214	9.422	111.778	519.80
$\uparrow\downarrow\uparrow\downarrow$	PBE0	7.062	8.108	9.257	110.886	495.18
	HSE	7.063	8.112	9.262	110.897	495.82
AFM	GGA ¹	7.217	8.212	9.429	111.14	521.20
	GGA+U ¹	7.095	8.095	9.355	111.16	501.03
	$GGA+U+D2^{1}$	6.890	8.104	9.156	111.09	476.99
PM	XRD ²	6.876	8.113	9.162	109.54	481.67
	XRD ³	6.895	8.113	9.164	109.62	482.86
	XRD ⁴	6.887	8.108	9.156	109.54	481.59
	XRD ⁵	6.901	8.108	9.176	109.65	483.53

¹ Theory: PBE, also including Hubbard-*U* and Van der Waals D2 corrections, Ref. [23]. ² Experiment: X-ray diffraction (XRD), powder, Cu K α , Ref. [15]. ³ Experiment: XRD, single-crystal, Mo K α , Ref. [14]. ⁴ Experiment: XRD, powder, Cu K α , Ref. [22]. ⁵ Experiment: XRD, nanocrystals, Cu K α , Ref. [23].

Table 2. Calculated Cu–O–Cu bond angles ($\angle_{Cu-O-Cu}$), Cu–Cu distances (d_{Cu-Cu}), and volumes of [CuO₅] and [PO₄] polyhedra in α -Cu₂P₂O₇.

State	Functional	∠ _{Cu−O−Cu} (°)	$d_{\operatorname{Cu}_1-\operatorname{Cu}_2}$ (Å)	d _{Cu2} -Cu3 (Å)	V _[CuO5] (Å ³)	$V_{[\mathrm{PO}_4]}$ (Å ³)
FM	PBE	101.735	3.124	3.354	6.905	1.921
$\uparrow\uparrow\uparrow\uparrow$	PBE0	100.015	3.052	3.257	6.580	1.837
	HSE	99.996	3.054	3.261	6.604	1.838
AFM-1	PBE	101.745	3.122	3.356	6.892	1.920
$\downarrow\downarrow\uparrow\uparrow\uparrow$	PBE0	100.322	3.054	3.262	6.533	1.834
	HSE	100.350	3.059	3.261	6.553	1.836
AFM-2	PBE	101.614	3.120	3.359	6.906	1.919
$\downarrow\uparrow\uparrow\downarrow$	PBE0	100.284	3.055	3.259	6.532	1.836
	HSE	100.301	3.056	3.266	6.558	1.835
AFM-3	PBE	100.290	3.092	3.359	6.928	1.918
↑↓↑↓	PBE0	100.022	3.047	3.266	6.541	1.833
	HSE	100.028	3.049	3.267	6.551	1.835

For the obtained parameters of Cu–O–Cu paths, competing exchange interactions may be expected to exist along the shortest Cu–Cu distance, giving rise to four possible magnetic configurations FM, AFM-1, AFM-2, and AFM-3 shown in Figure 1. Experimentally, α -Cu₂P₂O₇ is antiferromagnetic at cryogenic temperatures [12,23–26] and Curie-Weiss

paramagnetic (PM) at room temperature, with an effective paramagnetic moment of 1.89 μ_B corresponding to spin-1/2 moment on each Cu²⁺ ion [12].

Another structural degree of freedom is related to the $[P_2O_7]^{4-}$ polyhedron, consisting of two corner-sharing $[PO_4]^{3-}$ tetrahedra, as shown in Figure S2. The structure of $[PO_4]^{3-}$ polyhedron may be perturbed by changing the angle between these two $[PO_4]^{3-}$ tetrahedral sub-units and the values of P–O bond lengths. The P–O(1)–P bond angle is calculated to be about 154.736°, which is consistent with the experimental value of 157° [15]. The obtained inner and outer P–O bond lengths for $[P_2O_7]^{4-}$ polyhedron are 1.585 Å and 1.539 Å, respectively, in agreement with the corresponding values of 1.58 Å and 1.53 Å measured in Ref. [15]. The calculated volume of $[PO_4]^{3-}$ tetrahedron is about 1.9 Å³. Intriguingly, the lattice parameters in Tables 1 and 2 show very slight differences among the four studied magnetic configurations. It is worth mentioning that, compared with the PBE functional, all of these values shrink when a hybrid density functional, PBE0 or HSE, is used.

The calculated formation energies (ΔE_f and ΔE_f^{ox}) of α -Cu₂P₂O₇ in the four considered states of magnetic order are collected in Table 3. The obtained negative values indicate an exothermic formation process and the thermodynamic stability of the compound. By comparing the experimental and calculated formation energies ΔE_f listed in Table 3, one may get an impression that PBE works slightly better than the hybrid functionals for α -Cu₂P₂O₇. However, this is due to the fact that the energies of substances with very different types of chemical bonding are involved into Equation (1), so that the errors of DFT functionals do not cancel out. However, the experimental result for the enthalpy of formation of α -Cu₂P₂O₇ from the binary oxides at 298 K, ΔE_f^{ox} , is -279.0 ± 1.4 kJ/mol [22] while the calculated values (for the ground-state AFM-2 structure) using the PBE, PBE0, and HSE functional translate into -145.8, -252.2 and -252.8 kJ/mol, respectively. One can clearly see that hybrid functionals PBE0 and HSE give formation energy values that are consistent with the experimental result for α -Cu₂P₂O₇, while the value derived using a semi-local PBE functional is considerably off.

Table 3. Calculated formation energy ΔE_f (eV/f.u.), formation energy from oxides E_f^{ox} (eV/f.u.), band gap E_g (eV), and effective atomic charges ΔQ_{Cu} , ΔQ_P , and ΔQ_O , in α -Cu₂P₂O₇. Elementary charge units (*e*) are used; negative charge values denote a lack of electrons. Previous experimental and theoretical values are quoted for comparison.

State	Functional	ΔE_f	ΔE_f^{ox}	Eg	ΔQ_{Cu}	$\Delta Q_{ m P}$		Δ(2o	
FM	PBE	-22.616	-1.416	0	-1.19	-3.59	1.36	1.35	1.51	1.32
$\uparrow\uparrow\uparrow\uparrow$	PBE0	-24.453	-2.534	3.784	-1.35	-3.74	1.45	1.44	1.56	1.42
	HSE	-26.741	-2.562	3.084	-1.35	-3.74	1.45	1.44	1.56	1.42
AFM-1	PBE	-22.671	-1.475	0.390	-1.19	-3.64	1.39	1.36	1.52	1.32
$\downarrow\downarrow\uparrow\uparrow\uparrow$	PBE0	-24.519	-2.604	4.344	-1.35	-3.79	1.46	1.46	1.58	1.42
	HSE	-26.785	-2.610	3.566	-1.35	-3.79	1.46	1.46	1.58	1.42
AFM-2	PBE	-22.704	-1.511	0.730	-1.19	-3.64	1.39	1.36	1.52	1.32
$\downarrow\uparrow\uparrow\downarrow$	PBE0	-24.530	-2.614	4.670	-1.35	-3.79	1.46	1.46	1.58	1.42
	HSE	-26.796	-2.620	3.966	-1.35	-3.79	1.46	1.46	1.58	1.42
AFM-3	PBE	-22.649	-1.447	0.362	-1.20	-3.65	1.39	1.36	1.52	1.33
↑↓↑↓	PBE0	-24.530	-2.605	4.395	-1.35	-3.79	1.46	1.46	1.58	1.42
	HSE	-26.785	-2.611	3.683	-1.35	-3.79	1.46	1.46	1.58	1.43
	Previous studies	-21.725 ¹	-2.892 ¹	2.85 ² , 3.17 ³ , 3.36 ⁴ , 3.79 ⁵						

¹ Experiment (calorimetry) Ref. [22]. ² Theory (GGA+*U*) Ref. [26]. ³ Theory (GGA+*U*) Ref. [23]. ⁴ Theory (LDA+*U*) Ref. [12]. ⁵ Experiment (UV-spectrometry) Ref. [17].

Notably, the calculated ΔE_f and ΔE_f^{ox} are the lowest for the AFM-2 ordered state as compared with the other three states of magnetic order, when calculated with any of

the PBE, PBE0, or HSE functionals. This demonstrates that AFM-2 is indeed the most stable ordered structure, which supports the findings of previous studies that α -Cu₂P₂O₇ exhibits an antiferromagnetic ordering bellow 22–27 K [12,23–26]. In particular, the ground-state energy (E_{tot}) of AFM-2 ordered state is smaller than that of FM state by 0.189, 0.158, or 0.116 eV (per primitive cell) when calculated using PBE, PBE0, or HSE functionals, respectively, see Table 4 for further details.

Table 4. Calculated total energy E_{tot} (eV per primitive cell), total magnetic moment M_{tot} (Bohr magnetons $\mu_{\rm B}$ per primitive cell), and local magnetic moments $M_{\rm Cu}$, $M_{\rm P}$, and $M_{\rm O}$ ($\mu_{\rm B}$) on the respective atoms in α -Cu₂P₂O₇. Previous theoretical data are also quoted for comparison [23].

State	Functional	E_{tot} (eV)	M_{tot} ($\mu_{ m B}/{ m Cell}$)	$M_{\rm Cu}$ ($\mu_{\rm B}$)	$M_{ m P}$ ($\mu_{ m B}$)	$M_{\rm O}~(\mu_{\rm B})$
FM ↑↑↑↑	PBE PBE0 HSE	-140.547 -189.559 -179.043	3.539 3.944 3.944	0.606 0.793 0.791	0.006 0.008 0.008	0.078 0.062 0.063
AFM-1 ↓↓↑↑	PBE PBE0 HSE	-140.664 -189.699 -179.140	0.000 0.000 0.000	$\pm 0.599 \\ \pm 0.791 \\ \pm 0.790$	$\pm 0.002 \\ \pm 0.002 \\ \pm 0.002$	$\pm 0.020 \\ \pm 0.033 \\ \pm 0.029$
AFM-2 ↓↑↑↓	PBE PBE0 HSE	-140.736 -189.717 -179.159	0.000 0.000 0.000	$\pm 0.579 \\ \pm 0.787 \\ \pm 0.785$	$\pm 0.003 \\ \pm 0.002 \\ \pm 0.002$	$\pm 0.034 \\ \pm 0.028 \\ \pm 0.028$
AFM-3 ↑↓↑↓	PBE PBE0 HSE	-140.609 -189.701 -179.140	0.000 0.000 0.000	$\pm 0.612 \\ \pm 0.789 \\ \pm 0.788$	$\pm 0.004 \\ \pm 00.004 \\ \pm 0.004$	$\pm 0.067 \\ \pm 0.052 \\ \pm 0.052$
FM AFM	GGA [23] GGA+U [23] GGA [23] GGA+U [23]	-140.567 -99.822 -140.598 -99.830		$0.554 \\ 0.840 \\ \pm 0.610 \\ \pm 0.838$		

3.2. Elastic Properties and Mechanical Stability of α -Cu₂P₂O₇

Before discussing the calculated elastic and other properties of α -Cu₂P₂O₇ in detail, it is instructive to demonstrate its mechanical stability. For a monoclinic structure, the Born criteria of mechanical stability [49,50] require that the following equations should be satisfied [51],

$$C_{ii} > 0 \ (i = 1, 2, 3, 4, 5, 6), \ C_{11} + C_{12} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0,$$

$$C_{33}C_{55} - C_{35}^2 > 0, \ C_{44}C_{66} - C_{46}^2 > 0, \ (C_{22} + C_{33} - 2C_{23}) > 0,$$

$$[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0,$$

$$\{2[a_1C_{15}C_{25} + b_1C_{15}C_{35} + c_1C_{25}C_{35}] - [d_1C_{15}^2 + e_1C_{25}^2 + f_1C_{35}^2]\} + g_1C_{35} > 0.$$

(6)

Here $a_1 = C_{33}C_{12} - C_{13}C_{23}$, $b_1 = C_{22}C_{13} - C_{12}C_{23}$, $c_1 = C_{11}C_{23} - C_{12}C_{13}$, $d_1 = C_{22}C_{33} - C_{23}^2$, $e_1 = C_{11}C_{33} - C_{13}^2$, $f_1 = C_{11}C_{22} - C_{12}^2$, and $g_1 = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23}$.

The calculated elastic constants for α -Cu₂P₂O₇ are collected in Table 5. According to Equation (6) and the obtained values, we can definitely conclude that α -Cu₂P₂O₇ is mechanically stable since the calculated elastic constants meet the Born stability criteria. The calculated elastic constants C_{11} , C_{22} and C_{33} are lower than 200 GPa, indicating that α -Cu₂P₂O₇ has a relatively weak deformation resistance along the *a*-, *b*- and *c*-axes. Also, the elastic constants C_{44} , C_{55} and C_{66} are calculated to be small. It can therefore be concluded that α -Cu₂P₂O₇ has a weak shear deformation resistance.

Table 5. Calculated elastic constants C_{ij} (GPa) of α -Cu₂P₂O₇.

State	<i>C</i> ₁₁	C ₂₂	C ₃₃	<i>C</i> ₄₄	C ₅₅	C ₆₆	<i>C</i> ₁₂	<i>C</i> ₁₃	C ₂₃	C ₄₆	<i>C</i> ₁₅	C ₂₅	C ₃₅
AFM-2	120.8	97.7	174.1	59.9	61.7	56.6	71.5	79.9	72.1	8.4	-34.1	-1.2	-43.5

Ab initio determination of mechanical properties of anisotropic crystalline materials is a formidable multi-scale problem. In this connection, it is common to make simplified qualitative judgments about the mechanical properties of materials using empirical relationships formulated in terms of directionally-averaged (polycrystalline) elastic moduli such as bulk modulus (B) and shear modulus (G). In our work, the elastic moduli of α -Cu₂P₂O₇ have been calculated using the Voigt-Reuss-Hill theory [52–54]. More details are presented in the Supporting information. The average Young's modulus (Y) and Poisson ratio (ν) are calculated through Y = 9BG/(3B+G) and $\nu = (3B/2G)/[2(3B+G)]$. The calculated averaged moduli and other indicators of mechanical properties are listed in Table 6. The averaged bulk modulus measures the resistance of a polycrystalline material to a volume change. The calculated Voigt-, Reuss-, and Hill-averaged bulk moduli *B* are 93.298 GPa, 80.624 GPa, and 86.961 GPa, respectively. Thus, α -Cu₂P₂O₇ has a relatively weak volume deformation resistance, which is consistent with the conclusions from the single-crystal elastic constants. The averaged shear modulus G reflects the shear deformation resistance of a polycrystalline material. The obtained values of Voigt-, Reuss-, and Hill-averaged shear moduli are close to each other, around 35 GPa, which shows that α -Cu₂P₂O₇ has relatively weak shear deformation resistance. The calculated averaged Young's moduli are 120.468 GPa, 80.112 GPa, and 100.533 GPa, indicating low elastic stiffness. In addition, the B/G ratio is a common parameter to judge the ductility of a material [55,56]. If the value of B/G is larger than 1.75, the material is expected to exhibit ductile behavior; otherwise, the material is expected to exhibit brittle behavior. It can be seen that the calculated B/G ratio for α -Cu₂P₂O₇ is greater than 1.75, indicating that the material should be ductile. Poisson's ratio is another indicator of the ductility of a material, predicting the material to exhibit ductile behavior if $\nu > 0.26$. The obtained values of ν indicate that α -Cu₂P₂O₇ should be ductile, in agreement with the analysis based on B/G ratio.

Table 6. Direction-averaged bulk modulus *B*, shear modulus *G*, Young's modulus *Y*, Poisson's ratio ν , bulk-to-shear modulus ratio (*B*/*G*), and hardness *H* of α -Cu₂P₂O₇ calculated according to Voigt, Reuss, and Hill approximations.

Droporty		Averaging Method:	
rioperty	Voigt	Reuss	Hill
B (GPa)	93.298	80.624	86.961
G (GPa)	46.882	30.018	38.450
Y (GPa)	120.468	80.112	100.533
(B/G)	1.990	2.686	2.262
ν	0.285	0.334	0.300
H (GPa)	6.413	3.326	4.819

3.3. Electronic and Magnetic Structure of α -Cu₂P₂O₇

The spin-resolved band structure of α -Cu₂P₂O₇ has been calculated to evaluate the exchange coupling using PBE, PBE0, and HSE functionals. As Figure S3a shows, the band structure calculated within PBE functional for α -Cu₂P₂O₇ in FM state is metallic. Specifically, the states at the Fermi level (chosen to be the zero of energy) belong to both spin-up and spin-down channels, while the states from just above the Fermi level to the top of the valence band have pure spin-down character (exhibit 100% spin polarization). It is well known that PBE functional tends to underestimate band gaps [57]; therefore, additional calculations using hybrid functionals PBE0 and HSE have been performed to get better estimates of the band gap, as depicted in Figure S3 and Figure 2, respectively.



Figure 2. Fat band structures for α -Cu₂P₂O₇ in (**a**) FM spin-up channel, (**b**) FM spin-down channel, (**c**) AFM-1, (**d**) AFM-2, and (**e**) AFM-3 magnetic states calculated within HSE density functional. The zero energy is chosen at the highest occupied level at 0 K. The inset in panel (**a**) shows the BZ shape and paths used in the electronic and phonon spectrum calculations.

Surprisingly, a band gap as large as 3.784 eV and 3.084 eV opens up in the electronic structure of FM α -Cu₂P₂O₇ upon going from PBE to, respectively, PBE0 and HSE functionals. In particular, we observe a sizeable enhancement of the band gap value in the spin-down channel. According to a previous study, the local Coulomb interaction *U* in GGA+*U* or LDA+*U* calculations appears to produce a similar band gap opening in the electronic structure of FM α -Cu₂P₂O₇, indicating that the insulating ground state of α -Cu₂P₂O₇ is of the Mott type [12,23].

In the case of AFM-1 magnetic ordering, due to the shifts of the valence band maximum (VBM) and conduction band minimum (CBM) positions, the band gap values have been calculated to be 0.390 eV, 4.344 eV, and 3.566 eV within PBE, PBE0, and HSE functionals, respectively. The calculated band gap values for AFM-2 state of magnetic order are 0.730 eV, 4.670 eV, and 3.966 eV within PBE, PBE0, and HSE functional, respectively. Finally, the obtained band gap values for the AMF-3 state are 0.362 eV, 4.395 eV, and 3.683 eV within PBE, PBE0, and HSE functionals, respectively. All calculations that consider an antiferromagnetic order of Cu magnetic moments predict α -Cu₂P₂O₇ to be a semiconductor. Additionally, the same variation trend of the band structures is observed under PBE0 and HSE hybrid functional calculations. All these results are collected in Table 3. The band gap values calculated in this work using hybrid functionals agree reasonably well with the band gap values of 3.17 eV, 2.85 eV, 3.36 eV, and 3.80 eV calculated previously using LDA+U and GGA+U approaches [12,16,17,26]. But as a whole, HSE results seem to be in better agreement with the experiment than PBE0 results. Intriguingly, the total energy calculations show that the most favorable magnetic structure of α -Cu₂P₂O₇ is AFM-2, for which the largest band gap value is obtained no matter which functional (PBE, PBE0 or HSE) is used. Besides, the fat band structures calculated within HSE functional are depicted in Figure 2. They are resolved into the atoms to gain more physical insights into the electronic structure variations, in which blue-, cyan- and red-colored balls denote the contribution by Cu, P, and

O atoms, respectively. Similar to the four magnetic states, one finds that the valence bands are mainly dominated by O atoms with little contribution from Cu atoms. In contrast, the conduction bands are dominated by hybridized states of Cu and O atoms. What makes FM ordering special is that the conduction band states, in that case, are completely in the spin-down channel and belong to both Cu and O atoms, as shown in Figure 2b. It is worth mentioning that the hybridization of Cu and O atoms at the bottom of the conduction band of AFM-2 configuration is so strong that it produces an almost flat level, which leads to the smallest magnetic moments on Cu atoms, as shown in Figure 2d. Relative to that case, the exchange coupling of Cu and O atoms is weak and split into wider band energy regions in the cases of FM, AFM-1, and AFM-3 ordering. Based on above discussion one can conclude that α -Cu₂P₂O₇ is an antiferromagnetic semiconductor with a band gap of ~3.96 eV.

To get a deeper insight into the band structure, the spin-polarized total density of states (TDOS) and partial density of states (PDOS), computed using HSE functional, have been plotted together in Figure 3. In all the four cases of magnetic ordering, the broad oxygen bands are located between -9 and 0 eV, with an admixture of Cu 3d band states above -5.5 eV corresponding to the [CuO₅] pyramid. Specifically, the top of the valence band (VBM) is primarily composed of O-2*p* electron states with a slight admixture of Cu-3*d* states, particularly Cu $d_{y^2-y^2}$ orbital states. Oppositely, the CBM is mainly composed of Cu-3d electron states hybridized with O-2p states, especially in the AFM-2 case, which is resolved as the magnetically active orbital [11]. This relevant hybridization was identified using Wannier functions and LDA for Cu $d_{x^2-y^2}$ states [11,58]. Figure S5 zooms into the magnetic layers of [Cu₂O₆] structural dimers, containing two edge-sharing [CuO₄] plaquettes, which are separated from each other by nonmagnetic [PO₄] tetrahedra in α -Cu₂P₂O₇. More exactly, the spacer layers consist of $[P_2O_7]$ pyrophosphate groups formed by joining two $[PO_4]$ tetrahedra into a corner-sharing structural unit. Thus, the magnetic orbital lies in the plane of $[CuO_4]$ plaquette which for two possible magnetic coupling pathways, i.e., $Cu_1-O_1-Cu_2$ and Cu_1 – O_2 – Cu_2 pathways.

Figure 3. (**a**–**d**) Electronic total density of states (TDOS) and atom-projected density of states for α -Cu₂P₂O₇ in the four studied states of magnetic order, as calculated within HSE density functional. The zero of energy is chosen at the highest occupied level at 0 K.

The charge density cross-sections along the (-1.5, 1, -2.5) plane for $[Cu_2O_6]$ structural dimers in α -Cu₂P₂O₇ at 0.3 $e/Å^3$ are presented in Figure S6 for the four different magnetic states considered in this work. The covalent bonding component between Cu and O atoms can be clearly seen as streaks of the charge density, which may be attributed to the overlap and hybridization of Cu-3*d* and O-2*p* orbitals. The Bader analysis [59] shows the transfer of electrons from Cu and P cations to be about 1.35 *e* and 3.78 *e*, respectively. In comparison, the nearest O ion gains 1.42 *e*, indicating that the covalent and ionic contributions to Cu–O and P–O bonding are significant. More details can be found in Table 3.

3.4. Magnetic Properties of α -Cu₂P₂O₇

The alignment of magnetic moments arises from a competition between two physical mechanisms, the intraatomic exchange splitting and the interatomic interactions involving Cu 3d states. The magnitude of the magnetic moment increases with the strength of the exchange interaction. As shown in Table 2 and Figure 4, the shortest Cu–Cu separation distance of 3.056 Å, occurs between Cu_1 and Cu_2 ionic positions, as well as between Cu_3 and Cu_4 positions in the structure. For comparison, the bond length between Cu_2 and Cu_3 positions is 3.261 A. The short interatomic distance is expected to result in a strong direct interaction between the open 3d shells of these Cu^{2+} ions. The unoccupied Cu 3d states contribute to the narrow conduction band lying at about 4 eV in Figure 2d that forms a sharp DOS peak at the same energy in Figure 3c. All calculated information about the total and partial magnetic moments is collected in Table 4. Previously calculated values of magnetic moments are also given for comparison. With regards to FM ordering, the conduction bands come totally from spin-down states, with the dominant contribution due to Cu 3d states with a slight exchange splitting, as shown in Figure 2b. The splitting signifies a higher magnetic moment of the Cu atom. Within HSE functional the partial magnetic moments of Cu, P, and O in the FM case of orders are calculated to be 0.791 μ_B , 0.008 μ_B and 0.063 μ_B , respectively. The spin density in the interstitial region is rather small: it adds up to about 0.12 electrons per primitive cell in the calculations employing HSE functional. The total magnetic moment of the FM state is 3.944 μ_B per primitive cell, which is close to the integer value corresponding to one *d*-orbital hole per each of the four Cu^{2+} ions in the cell. For comparison, the local atomic moments are 0.785 μ_B for Cu, 0.002 μ_B for P, and 0.028 μ_B for O in AFM-2 ordered state, in which the net magnetic moment is 0 μ_B since the total DOS is symmetrical in the spin up and spin down channels. As Table 4 shows, the magnetic moments obtained in this work are in good agreement with the results of previous GGA+U calculations [23]. The local magnetic moments computed in this work are characteristic of Cu oxidation state 2+, which is in line with the paramagnetic moment of 0.15 emu/g [60] or 1.89 μ_B [12] experimentally reported for Cu₂P₂O₅ in the rage from -123 to +127 circC. Some nanocrystalline specimens at room temperature have been found to exhibit a weak ferromagnetic or superparamagnetic response to an applied strong magnetic field [17,60]. Unfortunately, no experimental data on local moments are available for the ordered antiferromagnetic state.

Theoretically, β -Cu₂V₂O₇ has been proposed to be a quasi-one-dimensional spin system composed of magnetic Cu²⁺ ions and a local magnetic moment of 0.73 μ_B per Cu atom was obtained from GGA+U calculations [61]. It is consistent with the values calculated in this work for α -Cu₂P₂O₇, due to structural similarities between the two phases where the Cu^{2+} ions are arranged into the [CuO₄] plaquettes linked via two corner-sharing [PO₄] tetrahedra. For comparison, the shortest Cu–Cu distance is of 2.9974 Å in α -Cu₂V₂O₇, which is slightly shorter than the Cu_1 – Cu_2 (or Cu_3 – Cu_4) bond length of 3.056 Å calculated here for α -Cu₂P₂O₇ in AFM-2 ordered state, see Figure 4. The length of the next-nearest neighbor bond, Cu₂–Cu₃, is 3.266 Å as obtained here from HSE functional calculations for α -Cu₂P₂O₇ in AFM-2 state. From Figure S6, one can see that the covalent component of bonding between Cu and O ions is very pronounced; the effect facilitates itself in the form of electron density streaks connecting the neighboring atoms and may be mainly attributed to the hybridization between Cu-3d and O-2p atomic orbitals upon the formation of the chemical bond. Also, Figure 4 shows that electron density accumulates near the short Cu₁– Cu₂ bonds; somewhat weaker density accumulation may be seen near the longer Cu₂-Cu₃ bonds. Thus, chemical bonding produces $zig-zag -Cu_1-Cu_2-Cu_3-Cu_4$ - chains along the *b*-axis in the structure of α -Cu₂P₂O₇ with AFM-2 ordering. The occurrence of these chains provides valuable theoretical support and a qualitative explanation to the hypothesis that transition metal pyro compounds ($M_2X_2O_7$) are quasi-one-dimensional spin systems composed of magnetic Cu^{2+} ions, as proposed by Janson et al. [12] for α -Cu₂P₂O₇ and by Arongo et al. [11] for α -Cu₂As₂O₇.

Figure 4. (a) Atomic structure of α -Cu₂P₂O₇ for AFM-2 state in the (0, 1, 29.5) cross-section plane chosen for charge density calculation. (b) Contour plot of the charge density calculated in the (0, 1, 29.5) cross-section plane within HSE density functional. The isosurface level of the charge density is set at 0.3 *e*/Å³; the image is produced using VESTA [62]. The white solid and dotted lines indicate, respectively, the distances of 3.056 Å for $d_{Cu_1-Cu_2}$ bond and 3.266 Å for $d_{Cu_2-Cu_3}$ bond.

Contour plots (isosurfaces) of the spin density are depicted in Figure 5 for the studied magnetic configurations of α -Cu₂P₂O₇. The Figure clearly shows that the magnetic moments of α -Cu₂P₂O₇ arise from Cu atoms; the O and P atoms are essentially nonmagnetic and the spin density in the interstitial region is negligible. This is in accordance with the above-discussed results on the calculated magnetic moments. Spin densities for these four cases look similar: the colored clouds, indicating loci of accumulated spin-up and spin-down density, are almost identical for the different Cu positions. Particularly, the spin density along the Cu chains is localized in one orbital, i.e., $d_{x^2-y^2}$. Besides, one can see small clouds of spin density accumulated on O atoms, which is of importance for opening the superexchange channels like $Cu_1 - O_1 - Cu_2$ and $Cu_1 - O_2 - Cu_2$. Based on the above discussion, we can generally conclude that all four studied cases of magnetic ordering are reasonable with the consideration of electron interactions of each Cu atom with its first, second, and third nearest-neighbor atoms. After a more comprehensive analysis, we can conclude that the energetically preferable magnetic state in α -Cu₂P₂O₇ is AFM-2 ordering with quasi-one-dimensional antiferromagnetic $-Cu_1-Cu_2-Cu_3-Cu_4$ - chains along the b axis, in which two identical Cu-O-Cu paths make an angle of 100.301° to each other.

Figure 5. Spin density of α -Cu₂P₂O₇ in (**a**) FM, (**b**) AFM-1, (**c**) AFM-2 and (**d**) AFM-3 states of magnetic order, as calculated within HSE density functional. The isosurface level of the charge density is set at 0.2 $e/Å^3$; the image is produced using VESTA [62].

3.5. Phonon Dispersion Curves and Lattice Thermodynamic Properties

In addition to thermodynamic stability and mechanical stability, dynamical stability can also decide the structural stability of a material. Thus the phonon dispersion curves along the Y– Γ –A–M– Γ –L–N directions in the BZ have been calculated for the lowest-energy AFM-2 configuration using PBE functional at the PBE-optimized volume and are displayed in Figure 6a; the corresponding phonon density of state (PhDOS) is plotted in Figure 6b, see also Figure 2a for BZ path notations. It can be seen that there are no imaginary phonon frequencies, implying the dynamical stability of α -Cu₂P₂O₇ which depends on the vibration frequencies of all atoms in the material. The entire phonon spectrum consists of five separate frequency bands. The low-frequency band below 12 THz includes the acoustic and optical branches of vibrations involving all ions, Cu, P, and O. The broad optical band between 13 and 18 THz may be associated with bending modes of pyrophosphate [P₂O₇]^{4–} groups consisting in changing the P–O–P bridge angle. Then there occurs a distinct gap in the phonon dispersion relations with a narrow vibrational band at about 20 THz associated with stretching modes of the P–O–P bridge. The two high-frequency bands in the range from 25 to 34 THz above the gap are mainly due to O–P bond stretching modes.

Figure 6. Phonon dispersions (**a**) and phonon density of states (**b**) of α -Cu₂P₂O₇, as calculated within PBE density functional. For BZ path notations, see Figure 2.

Temperature dependencies of the total energy, Helmholtz free energy, entropy, and specific heat contributions from the lattice vibrations have been evaluated by integrating the phonon density of states obtained from the interaction force constants calculated in the quasi-harmonic approximation (QHA) [56,63]. In particular, the Helmholtz free energy (F) as a function of temperature (T) and volume (V) is expressed as following equation,

$$F(V,T) = E(V) + F_{\rm ph}(V,T) + F_{\rm ele}(V,T),$$
(7)

where E(V) is the electronic ground-state total energy of the system, $F_{ph}(V, T)$ denotes the phonon-free energy, and $F_{ele}(V, T)$ is the electronic excitation energy at a given unit cell volume (*V*) and temperature (*T*). For wide-band-gap semiconductors at moderate temperatures, the electronic free energy contribution may safely be neglected. Under the QHA, the phonon contributions to Helmholtz free energy F(V, T), the internal energy (*E*), and the vibrational entropy (*S*) can be obtained from PhDOS g(ω) using the following formulas [64],

$$F(V,T) = 3nNk_{\rm B}T \int_0^\infty g(\omega) \ln[2\sinh(\frac{\hbar\omega}{2k_{\rm B}T})]d\omega, \tag{8}$$

$$E(V,T) = 3nN\frac{\hbar}{2}\int_0^\infty \omega \coth\left(\frac{\hbar\omega}{2k_{\rm B}T}\right)g(\omega)d\omega,\tag{9}$$

$$S(V,T) = 3nNk_{\rm B} \int_0^\infty \left[\frac{\hbar\omega}{2k_{\rm B}T} \coth\left(\frac{\hbar\omega}{2k_{\rm B}T}\right) - \ln\{2\sinh\left(\frac{\hbar\omega}{2k_{\rm B}T}\right)\}\right]g(\omega)d\omega, \tag{10}$$

where $\omega = \omega(V)$ stands for the frequency of the phonon mode calculated at a primitive cell volume V, $g(\omega)$ is the phonon density of state with the norm $\int_0^{\infty} g(\omega)d\omega = 1$. F(V,T) and E(V,T) at zero temperature are both equal to the zero-point energy, which is given by $F_0 = E_0 = 3nN \int_0^{\infty} \frac{\hbar \omega}{2} g(\omega)d\omega$, where *n* is the number of atoms per primitive cell, *N* is the number of primitive cells. Here \hbar and $k_{\rm B}$ are the Plank constant and the Boltzmann constant, respectively.

The internal energy *E*, Helmholtz free energy *F* and entropy *S* of α -Cu₂P₂O₇, calculated in the temperature range of 0...1000 K using a 2 × 2 × 1 supercell (*Z* = 8) and expressed per mole of Cu₂P₂O₇ molecules at the molecular volume of 130.268 Å³, are shown in Figure 7a–c, respectively. Due to the vibrational contributions, *E* and *S* increase gradually with increasing the temperature, while *F* exhibits a non-linear decrease. Besides, the calculated zero-point energy of α -Cu₂P₂O₇ phase is *F*₀ = *E*₀ = 89.04 kJ/mol. (Note that the values of thermodynamic properties plotted in Figure 7 are expressed per mole of Cu₂P₂O₇ formula units).

A critical parameter to understand the thermal behavior of α -Cu₂P₂O₇ is the heat capacity at a constant volume, which can be expressed as

$$C_V = \frac{\partial F}{\partial T} = k_{\rm B} \int_0 d\omega g(\omega) (\frac{\hbar\omega}{k_{\rm B}T})^2 \frac{\exp(\frac{\hbar\omega}{k_{\rm B}T})}{[\exp(\frac{\hbar\omega}{k_{\rm B}T}) - 1]^2}.$$
(11)

The calculated temperature-dependent heat capacity of α -Cu₂P₂O₇ is shown in Figure 7d. One can see that C_V increases sharply at low temperatures (0–300 K). Then C_V increases smoothly up to 270 J/K per mole of Cu₂P₂O₇ formula units.

Figure 7. Temperature-dependent (**a**) total (internal) energy *E*, (**b**) Helmholtz free energy *F*, (**c**) entropy *S* and (**d**) heat capacity C_V of α -Cu₂P₂O₇ calculated per mole (of formula units) at a molecular volume of 130.268 Å³.

4. Conclusions

To summarize, we have carried out a comparative hybrid-density functional study (using PBE, PBE0, and HSE functionals) of electronic structure, magnetic ordering, phonon dispersion relations, and thermodynamic properties of α -Cu₂P₂O₇. First of all, the calculated formation energy, cohesive energy, elastic constants, and phonon dispersion relations indicate that α -Cu₂P₂O₇ is mechanically and thermodynamically stable. The mechanical property indicators based on elastic moduli reveal that α -Cu₂P₂O₇ should exhibit a ductile behavior with a relatively weak volume deformation resistance and shear deformation resistance. Secondly, the spin-polarized calculations indicate that the FM, AFM-1, AFM-2, and AFM-3 magnetic configurations have rather similar electronic structures, except for some slight differences at the bottom of the conduction band where the hybridization between the electron states of Cu and O atoms in the AFM-2 structure is so strong that the conduction band is shaped almost like a flat level. Thus AFM-2 magnetic ordering produces the largest band gap of 3.966 eV and the smallest local magnetic moments on Cu atoms within HSE functional calculations. Correspondingly, the states at the valence band maximum are mainly dominated by O states with a small contribution due to Cu electron states, particularly from $\operatorname{Cu}-d_{x^2-v^2}$ orbital. Thirdly, by comparing the energies for the different types of magnetic ordering in α -Cu₂P₂O₇, we find that AFM-2 ordering is the most stable structure having the strongest antiferromagnetic interactions. Specifically, the proposed one-dimensional spin system in AFM-2 ordering originates from $-Cu_1-Cu_2-Cu_3-Cu_4-Cu_4$ chains along the *b* axis, in which there are two identical Cu-O-Cu paths, each forming a bond angle of 100.301°. Within HSE functional, the partial magnetic moments on Cu atoms in FM, AFM-1, AFM-2 and AFM-3 ordered states are 0.791 $\mu_{\rm B}$, $\pm 0.790 \ \mu_{\rm B}$, $\pm 785 \ \mu_{\rm B}$ and $\pm 0.788 \ \mu_{\rm B}$, respectively. Fourthly, phonon dispersion relations indicate that there are four ranges of vibrational frequencies: (1) 0–12 THz contributed by acoustic and optical modes involving Cu, P, and O atoms, (2) 13–18 THz mainly dominated by vibrations corresponding to bending of pyrophosphate groups; (3) a narrow band at 20 THz due to the stretching modes of a P–O–P bridge; (4) two bands in the range 25–34 THz due to O–P stretching modes. Our systematic study on structural stability, electronic and magnetic properties, and phonon dispersion relations of α -Cu₂P₂O₇ opens a way for further computational studies of related materials such as transition metal pyro compounds, M₂X₂O₇.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/app13010498/s1, Formalism based on Voigt-Reuss-Hill (VRH) approximation for the evaluation of direction-averaged bulk modulus (B) and shear modulus (G) [52–54]; Figure S1: Optimized crystal structures of (a) CuO and (b) P₂O₅; Figure S2: The local structure of a pyrophosphate group $[P_2O_7]^{4-}$ in α -Cu₂P₂O₇; Figure S3: Electronic energy band structures calculated using PBE functional for α -Cu₂P₂O₇ in (a) FM, (b) AFM-1, (c) AFM-2, and (d) AFM-3 magnetic states; Figure S4: Electronic energy band structures calculated using PBE0 functional for α -Cu₂P₂O₇ in (a) FM, (b) AFM-1, (c) AFM-2, and (d) AFM-3 magnetic states; Figure S5: Different representations of the Cu local environment: (a) the [CuO₅] pyramid and (b) the [CuO₄] distorted plaquette; Figure S6: Charge density in the (-1.5, 1, -2.5) plane with [Cu₂O₆] layer in α -Cu₂P₂O₇ in four different magnetic states calculated using HSE functional. The isosurface level of the charge density is set at 0.3 $e/Å^3$.

Author Contributions: Conceptualization, P.K.; methodology, X.Y.; software, P.K.; validation, X.Y. and P.K.; formal analysis, X.Y. and P.Z.; investigation, X.Y. and P.K.; resources, P.K.; data curation, X.Y.; writing—original draft preparation, X.Y.; writing—review and editing, P.K.; visualization, P.K. and P.Z.; supervision, P.K.; project administration, P.K.; funding acquisition, X.Y. and P.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was performed at the Vinnova Competence Centre "Hero-m 2i", funded jointly by the Swedish Governmental Agency for Innovation Systems (Vinnova, grant number 2016-00668), Swedish industry, the Swedish steel producers' association Jernkontoret, and KTH Royal Institute of Technology. P.K. acknowledges support by Svensk Kärnbränslehantering AB (SKB). X.Y. sincerely appreciates the support of National Natural Science Foundation of China (Grant No. 11705152 and 11974055) and by Stiftelsen för Tillämpad Termodynamik, Sweden.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in the article and supplementary material.

Acknowledgments: The computational resources are provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC) in Linköping, Sweden, and at the Center for High-Performance Computing (PDC) in Stockholm, Sweden, partially funded by the Swedish Research Council through grant agreement No. 2018-05973.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AFM	Antiferromagnetic
ΒZ	Brillouin zone
DFT	Density functional theory
DOS	Density of states
FM	Ferromagnetic
GGA	Generalized gradient approximation
HSE	Heyd-Scuseria-Ernzerhof hybrid functional
LDA	Local density approximation
PAW	Projector-augmented-wave
PBE	Perdew-Burke-Ernzerhof semi-local functional
PBE0	Perdew-Burke-Ernzerhof hybrid functional
PDOS	Partial density of states
PhDOS	Phonon density of states
PM	Paramagnetic
QHA	Quasi-harmonic approximation
TDOS	Total density of states
VASP	Vienna Ab initio Simulation Package
XRD	X-ray diffraction

References

- 1. Dosen, A.; Marinkovic, B.A. Negative thermal expansion and cationic migration in zeolite Y used in FCC catalysts. *Bull. Mater. Sci.* **2019**, *42*, 86. [CrossRef]
- In-noi, O.; Daorattanachai, P.; Rungnim, C.; Prasitnok, K.; Rungtaweevoranit, B.; Faungnawakij, K.; Khemthong, P. Insight into Fructose Dehydration over Lewis Acid α-Cu₂P₂O₇ Catalyst. *Chem. Nano Mat.* 2021, 7, 292–298.
- Li, S.Y.; Liu, Q.L.; Zhou, J.J.; Pan, T.; Gao, L.; Zhang, W.D.; Fan, L.; Lu, Y.Y. Hierarchical Co₃O₄ Nanofiber-Carbon Sheet Skeleton with Superior Na/Li-Philic Property Enabling Highly Stable Alkali Metal Batteries. *Adv. Funct. Mater.* 2019, 29, 1808847. [CrossRef]
- Agarwal, A.; Majumder, S.; Sankapal, B.R.; Multi-walled carbon nanotubes supported copper phosphate microflowers for flexible solid-state supercapacitor. *Int. J. Energy Res.* 2022, 46, 6177–6196. [CrossRef]
- Meganathan, K.L.; BoopathiRaja, R.; Parthibavarman1, M.; Sharmila, V.; Shkir, M.; Gaikwad, S.A.; Praveenkumar, M. Design and fabrication of Cu₂P₂O₇@Ppy electrode for extraordinary capacitance and long-term stability for ideal asymmetric supercapacitor application. *J. Mater. Sci. Mater. Electron.* 2021, 32, 24736–24747. [CrossRef]
- Agarwal, A.; Sankapal, B.R.; Ultrathin Cu₂P₂O₇ nanoflakes on stainless steel substrate for flexible symmetric all-solid-state supercapacitors. *Chem. Eng. J.* 2021, 422, 130131. [CrossRef]
- Zou, H.; Yang, X.Q.; Chen, B.; Du, Y.Y.; Ren, B.Y.; Sun, X.W.; Qiao, X.S.; Zhang, Q.W.; Wang, F. Thermal enhancement of upconversion by negative lattice expansion in orthorhombic Yb₂W₃O₁₂. *Angew. Chem. Int. Ed.* 2019, *58*, 17255–17259. [CrossRef]
- 8. Magnusson, H.; Frisk, K. Thermodynamic evaluation of the copper-rich part of the Cu–H–O–S–P system at low temperatures. *CALPHAD* **2014**, *47*, 148–160. [CrossRef]
- Li, Y.G.; Korzhavyi, P.A. Interactions of point defects with stacking faults in oxygen-free phosphorus-containing copper. J. Nucl. Mater. 2015, 462, 160–164. [CrossRef]
- Sang, J.; Wei, P.; Liu, T.; Lv, H.; Ni, X.; Gao, D.; Zhang, J.; Li, H. Zang, Y.; Yang, F.; et al. A Reconstructed Cu₂P₂O₇ Catalyst for Selective CO₂ Electroreduction to Multicarbon Products. *Angew. Chem.* 2022, 134, 202114238. [CrossRef]
- Arango, Y.C.; Vavilova, E.; Hafiez, M.A.; Janson, O.; Tsirlin, A.A.; Rosner, H.; Drechsler, S.L.; Weil, M.; Nenert, G.; Klingeler, R.; et al. Magnetic properties of the low-dimensional spin-1/2 magnet α-Cu₂As₂O₇. *Phys. Rev. B* 2011, *84*, 134430. [CrossRef]

- 12. Janson, O.; Tsirlin, A.A.; Sichelschmidt, J.; Skourski, Y.; Weickert, F.; Rosner, H. Long-range superexchange in Cu₂A₂O₇ (A = P, As, V) as a key element of the microscopic magnetic model. *Phys. Rev. B* **2011**, *83*, 094435. [CrossRef]
- 13. Shi, N.; Sanson, A.; Gao, Q.L.; Sun, Q.; Ren, Y.; Huang, Q.Z.; de Souza, D.O.; Xing, X.R.; Chen, J. Strong Negative Thermal Expansion in a Low-Cost and Facile Oxide of Cu₂P₂O₇. *J. Am. Chem. Soc.* **2020**, *142*, 3088–3093. [CrossRef] [PubMed]
- 14. Effenberger, H. Structural refinement of low-temperature copper(II) pyrophosphate. Acta Cryst. C 1990, 46, 691–692. [CrossRef]
- 15. Robertson, B.E.; Calvo, C. The crystal structure and phase transformation of α-Cu₂P₂O₇. Acta Cryst. **1967**, 22, 665–672. [CrossRef]
- Pogorzelec-Glaser, K.; Pietraszko, A.; Hilczer, B.; Poomska, M. Structure and phase transitions in Cu₂P₂O₇. *Phase. Transit.* 2006, 79, 535–544. [CrossRef]
- 17. Karaphun, A.; Chirawatkul, P.; Maensiri, S.; Swatsitang, E. Influence of calcination temperature on the structural, morphological, optical, magnetic and electrochemical properties of Cu₂P₂O₇ nanocrystals. *J. Sol.-Gel. Sci. Technol.* **2018**, *88*, 407–421. [CrossRef]
- 18. Yang, X.Y.; Lu, Y.; Zhang, P. First-principles study of native point defects and diffusion behaviors of helium in zirconium carbide. *J. Nucl. Mater.* **2015**, *465*, 161–166. [CrossRef]
- Ren, K.; Wang, K.; Zhang, G. Atomic Adsorption-Controlled Magnetic Properties of a Two-Dimensional (2D) Janus Monolayer. ACS Appl. Electron. Mater. 2022, 4, 4507–4513. [CrossRef]
- Ren, K.; Ma, X.; Liu, X.; Xu, Y.; Huo, W.; Li, W.; Zhang, G. Prediction of 2D IV–VI semiconductors: Auxetic materials with direct bandgap and strong optical absorption. *Nanoscale* 2022, 14, 8463–8473. [CrossRef]
- Bamberger, C.E.; Specht, E.D.; Anovitz, L.M. Crystalline Copper Phosphates: Synthesis and Thermal Stability. J. Am. Ceram. Soc. 1997, 80, 3133–3138. [CrossRef]
- 22. Le, S.N.; Navrotsky, A.; Pralong, V. Energetics of copper diphosphates Cu₂P₂O₇ and Cu₃(P₂O₆OH)₂. *Solid State Sci.* **2008**, *10*, 761–767. [CrossRef]
- Pastukh, S.; Laskowska, M.; Dulski, M.; Krzykawski, T.; Parlinski, K.; Piekarz, P. Ab initio studies for characterization and identification of nanocrystalline copper pyrophosphate confined in mesoporous silica. *Nanotechnology* 2021, 32, 415701. [CrossRef] [PubMed]
- 24. Stiles, J.A.R.; Stager, C.V. Magnetic Structure of Manganese Pyrophosphate and Copper Pyrophosphate. *Can. J. Phys.* **1972**, 50, 3079. [CrossRef]
- 25. Stiles, J.A.R.; Stager, C.V. Nuclear Magnetic Resonance in Antiferromagnetic Cu₂P₂O₇. Can. J. Phys. 1973, 51, 87. [CrossRef]
- 26. Pastukh, S.; Piekarz, P. Ab initio calculations of the structural and dynamical properties of copper pyrophosphate. *Proceedings* **2020**, *4*, 32.
- Kohn, W.; Sham, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 1965, 140, A1133. [CrossRef]
- Hammer, B.; Hansen, L.B.; Nørskov, J.K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* 1999, 59, 7413. [CrossRef]
- 29. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev.* B **1996**, *54*, 11169. [CrossRef]
- Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.
 [CrossRef]
- Perdew, J.P.; Ernzerhof, M.; Bruke, K. Rationale for mixing exact exchange with density functional approximations. J. Chem. Phys. 1996, 105, 9982. [CrossRef]
- 32. Ernzerhof, M.; Scuseria, G.E. Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional. J. Chem. Phys. 1999, 110, 5029. [CrossRef]
- Heyd, J.; Scuseria, G.E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. J. Chem. Phys. 2003, 118, 8207.
 [CrossRef]
- 34. Heyd, J.; Scuseria, G.E. Assessment and validation of a screened Coulomb hybrid density functional. *J. Chem. Phys.* 2004, 120, 7274. [CrossRef]
- 35. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. Phys. Rev. B 1976, 13, 5188. [CrossRef]
- Sanville, E.; Kenny, S.D.; Smith, R.; Henkelman, G. Improved grid-based algorithm for Bader charge allocation. *J. Comput. Chem.* 2007, 28, 899–908. [CrossRef]
- 37. Togo, A.; Tanaka, I. First principles phonon calculations in materials science. Scr. Mater. 2015, 108, 1–5. [CrossRef]
- Ewing, M.B.; Lilley, T.H.; Olofsson, G.M.; Ratzsch, M.T.; Somsen, G. Standard quantities in chemical thermodynamics. Fugacities, activities and equilibrium constants for pure and mixed phases (IUPAC Recommendations 1994). *Pure Appl. Chem.* 1994, 66, 533–552. [CrossRef]
- 39. Paier, J.; Marsman, M.; Hummer, K.; Kresse, G.; Gerber, I.C.; Ángyán, J.G. Screened hybrid density functionals applied to solids. *J. Chem. Phys.* **2006**, 124, 154709. [CrossRef]
- Hosseini, S.M.; Movlarooy, T.; Kompany, A. First-principle calculations of the cohesive energy and electronic properties of PbTiO₃. Phys. B 2007, 391, 316e21. [CrossRef]
- 41. Yang, X.Y.; Yang, Y.; Lu, Y.; Sun, Z.Y.; Hussain, S.; Zhang, P. First-principles GGA+U calculation investigating the hydriding and diffusion properties of hydrogen in PuH_{2+x} , $0 \le x \le 1$. *Int. J. Hydrogen Energy* **2018**, 43, 13632–13638. [CrossRef]
- Pedroza, L.; da Silva, A.J.R.; Capelle, K. Gradient-dependent density functionals of the Perdew-Burke-Ernzerhof type for atoms, molecules, and solids. *Phys. Rev. B* 2009, *79*, 201106. [CrossRef]

- 43. Forsyth, J.B.; Brown, P.J.; Wanklyn, B.M. Magnetism in cupric oxide. J. Phys. C Solid State Phys. 1988, 21, 2917–2929. [CrossRef]
- 44. Watt, J.P. Hashin-Shtrikman bounds on the effective elastic moduli of polycrystals with monoclinic symmetry. *J. Appl. Phys.* **1980**, 51, 1520–1524. [CrossRef]
- 45. Zhang, P.; Wang, B.T.; Zhao, X.G. Ground-state properties and high-pressure behavior of plutonium dioxide: Density functional theory calculations. *Phys. Rev. B* 2010, *82*, 144110. [CrossRef]
- 46. Majtyka-Pilat, A.; Wojtyniak, M.; Laskowski, L.; Chrobak, D. Structure and Properties of Copper Pyrophosphate by First-Principle Calculations. *Materials* **2022**, *15*, 842. [CrossRef]
- 47. Hase, M.; Kohno, M.; Kitazawa, H.; Tsujii, N.; Suzuki, O.; Ozawa, K.; Kido, G.; Imai, M. Hu, X. 1/3 magnetization plateau observed in the spin-1/2 trimer chain compound Cu₃(P₂O₆OH)₂. *Phys. Rev. B* **2006**, *73*, 104419. [CrossRef]
- 48. Goodenough, J.B. Theory of the role of covalence in the Perovskite-Type Manganites [La, M(II)]MnO₃. *Phys. Rev.* **1995**, 100, 564. [CrossRef]
- 49. Born, M. On the stability of crystal lattices I. Proc. Camb. Philos. Soc. 1940, 36, 160–172. [CrossRef]
- 50. Grimvall, G.; Magyari-Köpe, B.; Ozoliņš, V.; Persson, K.A. Lattice instabilities in metallic elements. *Rev. Mod. Phys.* 2012, 84, 945–986. [CrossRef]
- Wu, Z.J.; Zhao, E.J.; Xiang, H.P.; Hao, X.F.; Liu, X.J.; Meng, J. Crystal structures and elastic properties of superhard IrN₂ and IrN₃ from first principles. *Phys. Rev. B* 2007, 76, 054115. [CrossRef]
- 52. Voigt, W. Lehrburch der Kristallphysik; Teubner: Leipzig, Germany, 1928.
- 53. Reuss, A.Berechnung der Fließgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. Z. Angew. Math. Mech. **1929**, *9*, 49–58. [CrossRef]
- 54. Hill, R. The elastic behaviour of a crystalline aggregate. Proc. Phys. Soc. Lond. A 1952, 65, 350. [CrossRef]
- 55. Pugh, S.F. XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Phil. Mag.* **1954**, 45, 823–843. [CrossRef]
- 56. Yang, X.Y.; Lu, Y.; Wei, Z.F.; Ping, Z. Mechanical, electronic, and thermodynamic properties of zirconium carbide from firstprinciples calculations. *Chin. Phys. B* 2015, 24, 116301. [CrossRef]
- Li, Y.G.; Korzhavyi, P.A. Physical and chemical properties of Cu (I) compounds with O and/or H. Dalton Trans. 2017, 46, 529–538. [CrossRef]
- 58. Eschrig, H.; Koepernik, K. Tight-binding models for the iron-based superconductors. Phys. Rev. B 2009, 80, 104503. [CrossRef]
- 59. Bader, R.F.W. Atoms in Molecules: A Quantum Theory; Oxford University Press: New York, NY, USA, 1990; p. 155.
- 60. Xiang, Y.; Hao, X.; Liu, X.; Wang, M.; Tian, J.; Kang, C.; Liang, E.; Zhang, W.; Jia, Y. Tailoring Thermal Expansion of (LiFe)_{0.5x}Cu_{2-x}xP₂O₇ via Codoping LiFe Diatoms in Cu₂P₂O₇ Oxide. *Inorg. Chem.* **2022**, *61*, 1504–1511. [CrossRef]
- Yashima, M.; Suzuki, R.O. Electronic structure and magnetic properties of monoclinic β-Cu₂V₂O₇: A GGA+U study. *Phys. Rev. B* 2009, 79, 125201. [CrossRef]
- Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Crystallogr. 2011, 44, 1272–1276. [CrossRef]
- Yang, X.Y.; Lu, Y.; Zhang, P. The temperature-dependent diffusion coefficient of helium in zirconium carbide studied with first-principles calculations. J. Appl. Phys. 2015, 117, 164903. [CrossRef]
- 64. Lee, C.; Gonze, X. Ab initio calculation of the thermodynamic properties and atomic temperature factors of SiO₂ *α*-quartz and stishovite. *Phys. Rev. B* **1995**, *51*, 8610–8613. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.