

Article

Crystal Structures of Al₂Cu Revisited: Understanding Existing Phases and Exploring Other Potential Phases

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Abstract: When processing single crystal X-ray diffraction datasets for twins of Al₂Cu sample synthesized by the high-pressure sintering (HPS) method, we have clarified why the crystal structure of Al₂Cu was incorrectly solved about a century ago. The structural relationships between all existing Al₂Cu phases, including the Owen-, θ -, θ' -, and Ω -Al₂Cu phases, were investigated and established based on a proposed pseudo Al₂Cu phase. Two potential phases have been built up by adjusting the packing sequences of A/B layers of Al atoms that were inherent in all existing Al₂Cu phases. The mechanical, thermal, and dynamical stability of two such novel phases and their electronic properties were investigated by first-principles calculations.

Keywords: high-pressure sintering; Al₂Cu; crystal structure; stability

1. Introduction

Al–Cu binary alloys are widely used in aerospace, automobile, and other fields, due to their high strength-to-weight ratio [1]. Among all compounds in the Al–Cu system, the Al₂Cu phase has been extensively investigated due its significant effect on the properties of Al–Cu alloys. It was reported that Al₂Cu adopts a tetragonal structure with $a = b = 4.28$ Å and $c = 2.40$ Å, as determined by Owen et al. through powder X-ray diffraction patterns [2] (hereafter named the Owen phase). Then, Jette et al. [3] suggested a larger tetragonal unit cell ($a = b = 6.052$ Å and $c = 4.878$ Å) should be used to describe the θ -Al₂Cu phase. Finally, Friauf [4] confirmed Jette’s results and provided the exact atomic positions of θ -Al₂Cu. During the next ninety years, it was again confirmed to have a tetragonal space group ($a = b = 6.067(1)$ Å and $c = 4.877(1)$ Å, S.G. $I4/mcm$) [5], which was generally accepted by the community [6,7]. The θ' -Al₂Cu phase is another very important strengthening phase in aluminum alloys [8], which is generally accepted to have a body centered tetragonal structure ($a = b = 4.04$ Å and $c = 5.80$ Å, S.G. $I4/mmm$) [9]. In addition, the structural information of the Ω -Al₂Cu phase has been hotly debated since its discovery and different structural models have been proposed [10–12]. The Ω phase is generally believed to have an orthorhombic structure ($a = 4.96$ Å, $b = 8.56$ Å, $c = 8.48$ Å), which is a distorted form of the tetragonal θ -Al₂Cu [10,13]. Although extensive experimental and simulation works have been carried out on the structural, electronic, physical properties of the above-mentioned (θ , θ' , Ω)-Al₂Cu precipitated as well as interface phases [6,7,14,15], knowledge on their structural relations are still quite limited.

Here, we report the data processing of diffraction data sets collected with a four-circle single crystal X-ray diffractometer (Bruker D8 venture, Bruker AXS GmbH, Karlsruhe, Germany) for a piece of Al–Cu sample. During indexing, solving, and refining of the synthesized Al–Cu phase, a pseudo Al₂Cu phase similar to that reported by Owen et al. [2] was proposed. The pseudo Al₂Cu phase changes to the θ -Al₂Cu phase if certain small number of reflections are carefully included during data processing. As will be illustrated, the pseudo Al₂Cu phase can be considered to be the average structure of all other

existing Al_2Cu phases (θ -, θ' - and Ω - Al_2Cu phase). Based on such a rule, two other potential Al_2Cu phases were built by rearranging the packing sequences of two atomic net planes encoded in all existing Al_2Cu phases. Meanwhile, the mechanical, dynamical stability, as well as the formation enthalpy and electronic properties of the proposed phases were investigated by first-principles calculations.

2. Materials and Methods

The Al_2Cu sample was discovered during efforts to prepare Al rich Al–Cu phase by mixing pure aluminum powder (indicated purity 99.8%) and copper powder (indicated purity 99.9%), in an atomic ratio of 6:1. Blended powders were then placed in a grinding tool of diameter 9.6 mm and were pressed into a tablet at about 4 MPa slowly and continuously for about five minutes. A cylindrical block 9.6 mm in diameter and 10 mm in height was obtained without cracks or deformations. The cylindrical block was encapsulated into an h-BN crucible covered by an h-BN gasket and wrapped in a graphite stove. Both ends of the graphite stove were filled with a pyrophyllite and dolomite composite medium and sealed by conducting steel rings. Finally, all of these components were put into a pyrophyllite rock that served as a pressure transition medium and were then inserted into a six-anvil high-pressure apparatus for high-pressure sintering (HPS) experiments (See Figure 1). Ultrahigh pressure 5 GPa was applied to the sample and heated to 1023 K for 30 min, cooled to 753 K for 2 h, and then rapidly cooled down to room temperature. Suitable pieces of crystals were selected for the single crystal X-ray diffraction measurements.

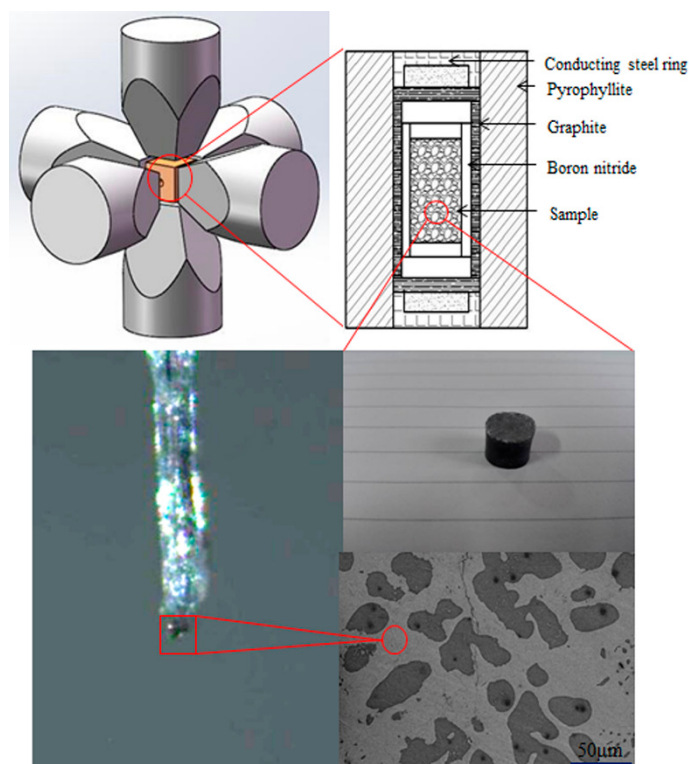


Figure 1. Schematic diagram of the high-pressure sintering (HPS) experiments with a six-anvil high-pressure apparatus. The zoomed-in figures are the layout of the crucible assembly, the cylindrical block of the sample and its scanning electron microscopy, the fragment of single crystal, respectively.

All density functional theory (DFT) based first-principles calculations in this work including geometry optimization, total energy, and electronic structure calculations, were performed by the Vienna Ab initio Simulation Package (VASP) [16,17]. The generalized gradient approximations (GGA) of the Perdew–Burke–Ernzerhof (PBE) type were adopted for the exchange correlation potential [18]. The projection-augmented wave (PAW) method [19] was applied to simulate the potentials between

electrons and ions. A plane wave basis was used to expand the wave functions with a cut-off energy of 500 eV. The Monkhorst–Pack scheme [20] was selected for the k-point sampling in the Brillouin zone ($7 \times 7 \times 9$ for both new phases). The static self-consistent convergence criteria were set at 1×10^{-6} eV/atom. The phonon spectrums were simulated using the supercell approach, by utilizing the Phonopy package [21].

3. Results and Discussion

3.1. Structural Relations of the Existing Phases

A piece of sample of size $0.050 \text{ mm} \times 0.055 \text{ mm} \times 0.090 \text{ mm}$ was selected for the single crystal X-ray diffraction measurements. The measured sample had a twin structure and it was found to quite easily neglect a small number of reflections (about 25%), while discriminating them from the two domains. Such reflections, as indicated by the red arrow in Figure 2a, resulted in a slightly different arrangement of reciprocal lattice points, as shown in Figure 2b. Surprisingly, with the incomplete reflections shown in Figure 2b, a pseudo Al_2Cu phase could be indexed and refined to a tetragonal structure with a $P4/mmm$ space group ($a = b = 4.279(2) \text{ \AA}$ and $c = 2.4337(13) \text{ \AA}$, see the supplementary materials), similar to those of the Owen-phase. Considering the Owen-phase was corrected to be the θ - Al_2Cu phase, it is of vital importance to clarify the relationship between the pseudo Al_2Cu phase, the Owen-phase, and other existing (θ , θ' , Ω)- Al_2Cu phases.

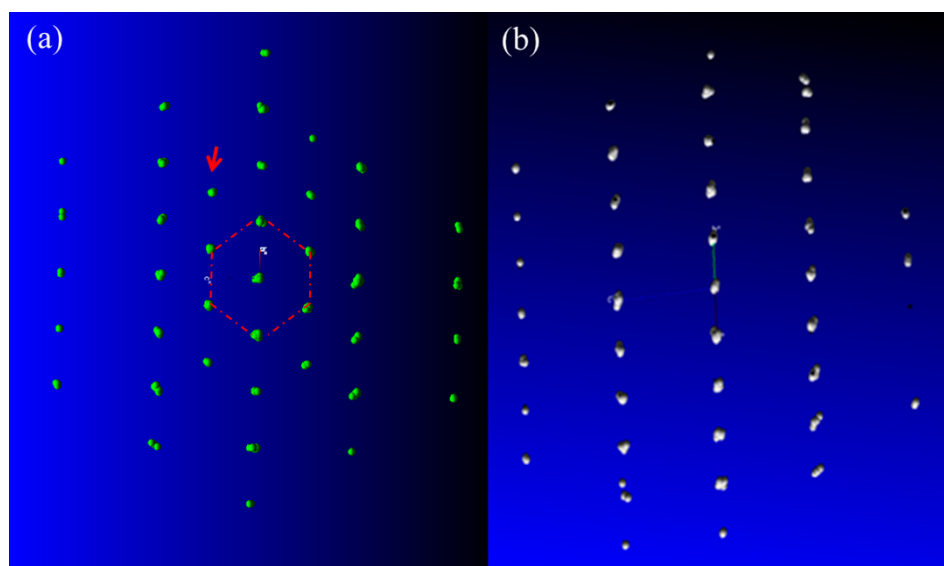


Figure 2. Projected reciprocal lattice points along the [110] direction of (a) θ - Al_2Cu phase and (b) the pseudo Al_2Cu phase.

First, let us study the relationship between the Owen- Al_2Cu and the θ - Al_2Cu phase. Figure 3a shows the established $2 \times 2 \times 2$ supercell of the Owen- Al_2Cu structure. It can be clearly observed that the established supercell can also be described by a θ - Al_2Cu -type unit cell (indicated by black dotted lines with $a = b = 4.28 \times \sqrt{2} = 6.053 \text{ \AA}$ and $c = 2.40 \times 2 = 4.80 \text{ \AA}$, see Figure 3b). The main difference between the Owen- Al_2Cu phase and that of the θ - Al_2Cu phase (shown in Figure 3c) lie in that the two adjacent layers, each formed by the four Al atoms in the θ - Al_2Cu phase, rotates around each other at $\delta = 45^\circ$, with clockwise and anti-clockwise rotation at $\delta/2 = 22.5^\circ$, compared to that of the Owen phase, as shown in Figure 3a–d. In the following, we name the layer represented by the four sky-blue and gray Al atoms in the θ - Al_2Cu phase as the A and B layer, respectively (in all cases, the Brown ball denotes the copper atom). Therefore, the Owen phase could be represented by larger tetragonal cells as suggested by Jette et al. [3], but it has a different arrangement of layers formed by Al atoms from

that of the θ -Al₂Cu phase. In other words, Al atoms are packed by same kind of layers along the c -axis in the Owen phase, but has repeating A-B layer sequences in the θ -Al₂Cu phase.

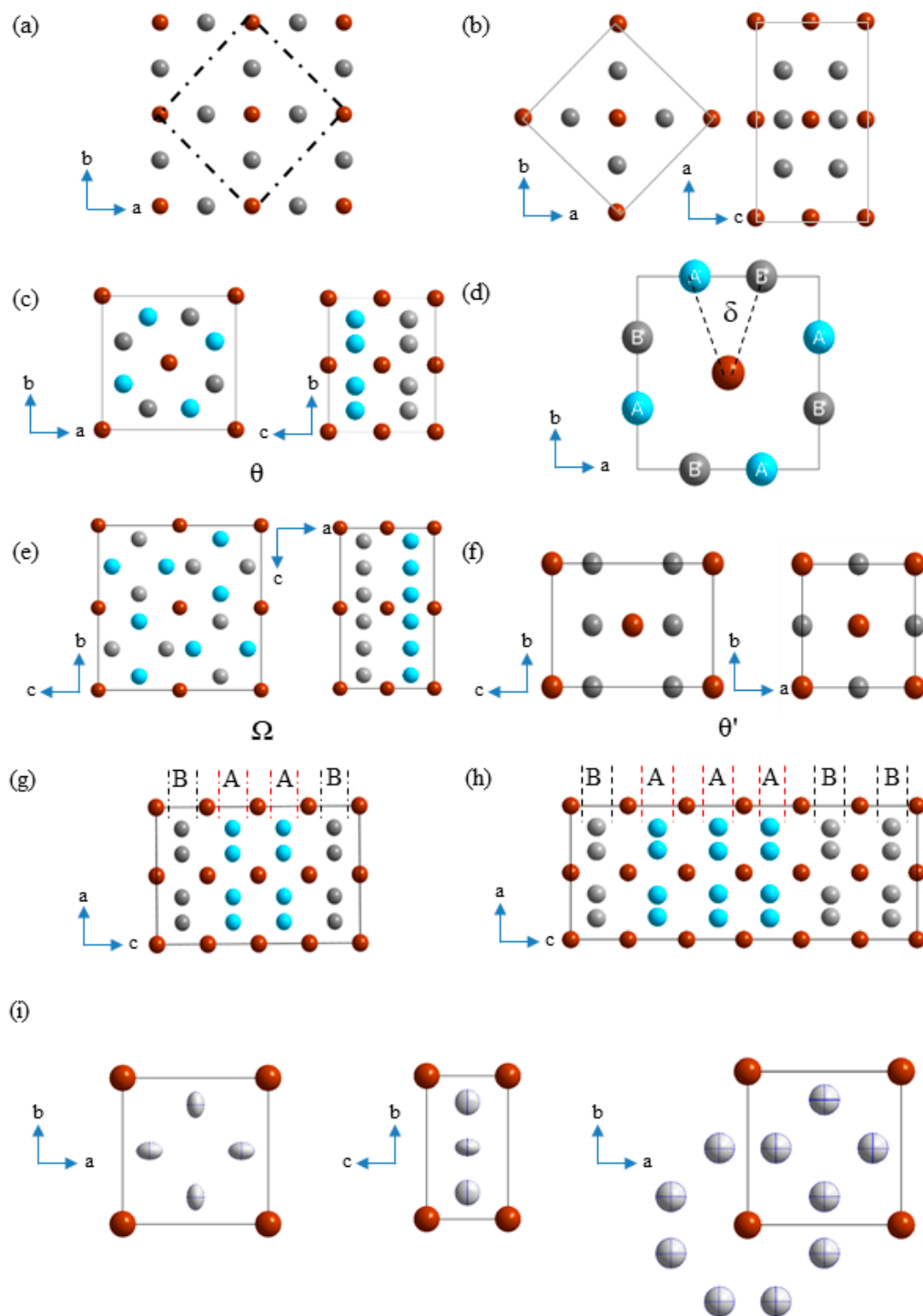


Figure 3. Crystal structure of the existing and potential Al₂Cu phases. (a) The 2 × 2 × 2 supercell of Owen-Al₂Cu; (b) a different description of the Owen phase as indicated by the black dotted lines in (a); (c) the θ phase; (d) the A and B layers each formed by four Al atoms in the unit cell, as shown along the c axis; (e) the Ω phase; (f) the θ' phase; (g) the M1 phase; (h) the M2 phase; and (i) the pseudo phase. (The Cu atoms are indicated in brown color balls in all cases, and the rest balls represent the Al atoms. The A and B layer discussed in the text are represented by sky-blue and gray Al atoms, respectively).

Second, let us consider the Ω -Al₂Cu phase which is a slightly distorted θ -Al₂Cu phase. To illustrate it clearly, the crystal structure of the Ω -Al₂Cu phase was established on the basis of previous reported results [10,13] (Figure 3e). It can be seen that the Al atoms are packed in A-B layer sequences in the Ω -Al₂Cu phase, similar to that of the θ -Al₂Cu phase. However, the Ω -Al₂Cu phase adopts a larger unit cell than that of the θ -Al₂Cu phase ($b \approx c \approx 6.067 \sqrt{2} \approx 4.28 \times 2 = 8.56 \text{ \AA}$; $a \approx 2.40 \times 2 = 4.80 \text{ \AA}$) and it contains four θ -Al₂Cu-type unit cell (two parallel and orthogonal to the rest two).

Third, let us turn to the simple but unique θ' -Al₂Cu phase. One can observe that the Al atoms are packed in B-B layer sequences in the θ' -Al₂Cu phase, similar to those in the Owen-Al₂Cu phase (see Figure 3f). However, the copper atoms occupy the body center and the vertex positions of the lattice in the θ' -Al₂Cu phase, resulting in a much larger c value and slightly smaller a or b values of lattice parameters ($a = b = 4.04 \text{ \AA}$ and $c = 5.80 \text{ \AA}$), as compared to that of the Owen-phase and the θ -Al₂Cu phase.

Last but not least, according to the refined crystal structure of the pseudo Al₂Cu phase, there are 4 equivalent Al atom positions in the unit cell and each have a site occupancy factor of 0.493 (see Figure 3i and see Figure S1 in the supplementary materials). As the distance between two Al atoms along each edge is too short (1.575 $\text{\AA}$), the Al atoms cannot simultaneously occupy two such positions. It can be easily acknowledged that the aforementioned A-B and B-B layer packing sequences are the two simplest packing arrangements of Al atoms, to avoid the meaningless short bond length of Al-Al atoms and to fit with a reasonable site occupancy factor less than 0.5. In other words, the pseudo Al₂Cu phase can be considered as the average structure of the θ - and Ω -Al₂Cu phase, while the Owen can be considered as the average structure of the pseudo Al₂Cu phase. Detailed crystallographic information of all existing Al₂Cu phases (Owen-, θ -, θ' - and Ω -Al₂Cu phase) are listed in Table 1.

Table 1. Crystallographic information of all existing Al₂Cu phases (the Owen-, θ -, θ' - and Ω phase) and two proposed potential Al₂Cu phases (M1 and M2 phase).

Phase	Space Group		Lattice Parameters			Wyckoff Positions				
	Symbol	Number	<i>a</i>	<i>b</i>	<i>c</i>	Atom Site	<i>x</i>	<i>y</i>	<i>z</i>	
Owen ^a	<i>P4/mmm</i>	123	4.28	4.28	2.405	Al1	2 <i>e</i>	1/2	0	1/2
						Cu1	1 <i>a</i>	0	0	0
Ω ^b	<i>Fmmm</i>	69	4.96	8.59	8.48	Al1	8 <i>h</i>	3/4	1/12	3/4
						Al2	8 <i>i</i>	3/4	3/4	11/12
θ ^c						Cu1	8 <i>f</i>	0	0	0
	<i>I4/mcm</i>	140	6.067	6.067	4.877	Al1	8 <i>h</i>	0.1581	0.6581	0
θ' ^d						Cu1	4 <i>a</i>	0	0	1/4
	<i>I4/mmm</i>	139	4.04	4.04	5.80	Al1	4 <i>d</i>	1/2	0	1/4
M1 ^e						Cu1	2 <i>a</i>	0	0	0
	<i>I4/mcm</i>	140	6.047	6.047	10.052	Al1	16 <i>l</i>	0.8405	0.3405	0.8855
M2 ^e						Cu1	4 <i>c</i>	0	0	1/4
						Cu2	4 <i>a</i>	0	0	0
	<i>I4/mcm</i>	140	6.008	6.008	15.445	Al1	16 <i>l</i>	0.8406	0.3406	0.5744
						Al2	8 <i>h</i>	0.8320	0.3320	3/4
Pseudo ^e						Cu1	8 <i>f</i>	0	0	0.1654
						Cu2	4 <i>a</i>	0	0	0
	<i>P4/mmm</i>	123	4.275	4.275	2.431	Al1	4 <i>l</i>	0.8159	1/2	1/2
						Cu1	1 <i>d</i>	0	0	0

^a Reference [2]; ^b Reference [10]; ^c Reference [5]; ^d Reference [9]; ^e Present work.

3.2. Potential Phases and Diffraction Patterns

Encouraged by discovering that the pseudo Al₂Cu phase has the average structure of all other existing Al₂Cu phases, we decided to further explore other potential Al₂Cu phases. According to the different packing sequences of A/B layers, two new structural models based on the pseudo Al₂Cu phase were built. In the M1 model, the Al atoms were arranged in the A-A-B-B layer sequences and the

copper atoms occupied the same positions as those in the θ -Al₂Cu phase (see Figure 3g). Consequently, the M2 model was built-up by packing Al atoms in the A-A-A-B-B layer sequences and arranging copper atoms as those in the θ -Al₂Cu phase (see Figure 3h). Although infinite number of new phases could be built-up in the same way, two such models are informative enough to investigate the stability and electronic properties of the Al₂Cu phases, which will be discussed in the following section. It was verified that the M1 and M2 models still adopted the tetragonal symmetry (S. G. *I4/mcm*), containing 16 Al atoms and 8 Cu atoms, and 24 Al atoms and 12 Cu atoms, respectively.

To observe the close relationship of these Al₂Cu phases, the power diffraction patterns ($2\theta = 0$ – 25°) of all existing and potential Al₂Cu phases were simulated. The powder diffraction patterns are shown in Figure 4. It can be seen that the two characterizing peaks of all phases between $2\theta = 9^\circ$ and 14° were indistinguishable, except those of the θ' phase. In the angle region beyond 14° , the diffraction peaks of the Owen phase, the pseudo phase, the θ phase, and the Ω -Al₂Cu phase were more comparable than those of other phases. There were only slight differences between the diffraction peaks of the Owen phase and the θ phase as indicated by the arrows inserted in Figure 4. Such observations might explain why the θ -Al₂Cu phase was initially incorrectly refined to be the Owen phase [2] and was easily mis-indexed to be the pseudo Al₂Cu phase during data processing of the present measured data sets. It also confirmed that the pseudo Al₂Cu phase could be considered as the average structure of the θ - and Ω -Al₂Cu phase, while the Owen might be considered to be the average structure of the pseudo Al₂Cu phase discussed before. For the potential M1 and M2 phases, it could be observed that there were some additional peaks in the $2\theta = 14^\circ$ and 16° region, implying that they are quite different phases from that of the θ phase and the Ω -Al₂Cu phase. Additional different reciprocal space information might be found in the projected simulated single crystal diffraction patterns (see the Supplementary Materials).

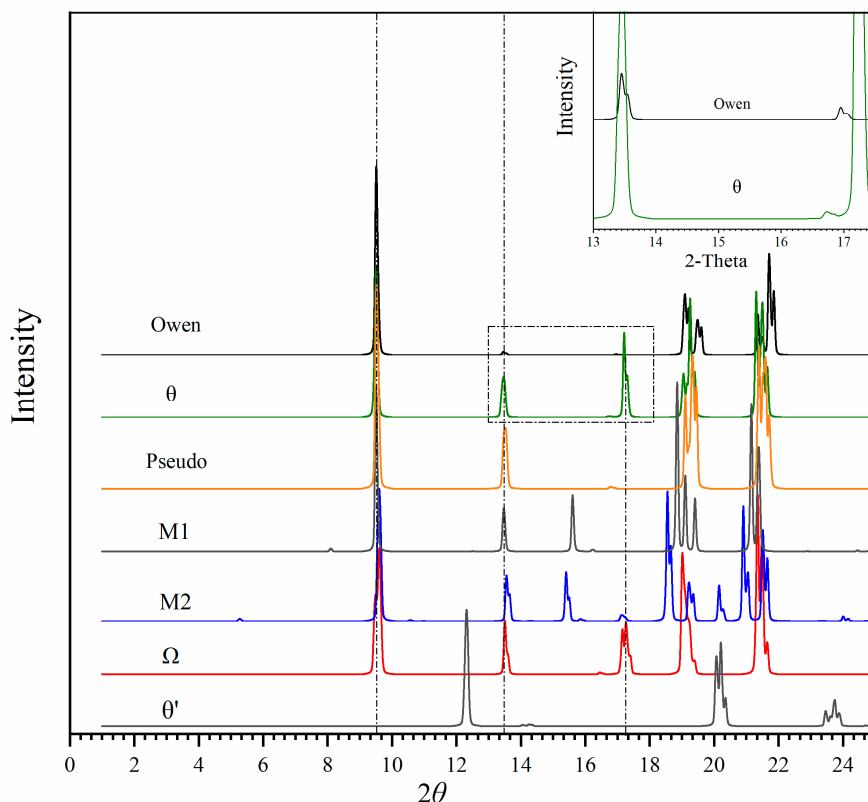


Figure 4. Simulated powder diffraction patterns for all existing and proposed Al₂Cu phases.

3.3. First-Principles Calculations

In this part, the mechanical, thermal and dynamic stability, as well as the electronic properties of the two proposed Al₂Cu phases have been investigated by first-principles calculations method. Table 2

shows the calculated cell parameters, elastic constants, and the enthalpy of formation of the Owen-, M1-, M2-Al₂Cu phases in the present work and for comparison, the θ -, θ' -, Ω - phases reported by previous studies are also mentioned. It can be seen that the a and b lattice values of the M1 and M2 phase agree well with those of the θ -Al₂Cu phase, implying that the packing of the A/B layers along the c direction has no effect on the in-plane arrangement of atoms. As mentioned earlier, the M1, M2, and the θ -Al₂Cu phase has the same average structure as the pseudo Al₂Cu phase, their lattice value of c is about double and triple of that of the θ -Al₂Cu phase.

As the enthalpy of formation (ΔH) indicates the forming ability of compounds, it was calculated according to the following formula [22]:

$$\Delta H = \frac{1}{x+y} (E_{tot} - xE_{solid}^{Al} - yE_{solid}^{Cu}) \quad (1)$$

where E_{tot} represent the total energy of the studied system, x and y represents the number of Al and Cu atoms, respectively. E_{solid}^{Al} and E_{solid}^{Cu} are the energy of each Al and Cu atom in their normal FCC unit cell. Negative enthalpy of formation indicates an exothermic process, and the lower the value of enthalpy of formation, the stronger the alloying ability [23]. From Table 2, one can find that all structures including the existing (θ , θ' , Ω)-Al₂Cu and the proposed M1 and M2 have negative enthalpy of formation, implying that they might show up under some favorable conditions, such as stable or metastable phases. It is necessary to note that the enthalpy of formation of both M1 and M2 are greater than those of the (θ , θ' , Ω)-Al₂Cu phases, suggesting that they are metastable phases. The enthalpy of formation of the Owen phase has a much higher value of $\Delta H = -0.025$ eV/atom than those of the M1/M2 phases, confirming that it is not the correct phase observed in previous experiments. From Table 2, one can also observe that the enthalpy of formation of the θ' -phase is slightly lower than that of the θ -phase and that of the Ω -phase is nearly equal to that of the θ -phase. However, precipitation experiments imply that the θ -phase should be the stable phase. It was found that the vibrational entropy reverses the energetic preference of the θ -phase and the θ' -phase at $T = 150$ – 200 K, which resolve the apparent discrepancy between theory and experiments [24].

Table 2. The cell parameters, elastic constants, and the enthalpy of formation of Al₂Cu (1924) θ , θ' , Ω , M1, M2.

Phase	Lattice Constants (Å)			C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	$\Delta H(\text{eV/atom})$
	a	b	c										
Owen	4.11	4.11	2.89	195.8		152.7	40.1		39.9	26.7	64.5		−0.025
θ ^{a,b}	6.05	6.05	4.87	156.3	−	170.2	31.9	−	40.9	83.2	65.3		−0.153
θ' ^{c,b}	4.04	4.04	5.80	158.9	−	160.3	48.0	−	40.5	56.8	60.9		−0.167
Ω ^{d,b}	4.96	8.56	8.48	161.7	159.2	164.2	42.5	41.9	49.9	65.7	69.6	80.8	−0.154
M1	6.04	6.04	10.0	81.7	−	176.0	31.6	−	42.9	27.3	53.0	−	−0.124
M2	6.00	6.00	15.44	99.7	−	147.9	18.6	−	36.3	32.9	43.4	−	−0.108

^a Reference [3]; ^b Reference [23]; ^c Reference [9]; ^d Reference [10].

The elastic constants can be used to estimate the resistance of crystals to external stress and to deduce the basic mechanical properties and structural mechanical stability. There are six independent elastic constants (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66}) for the tetragonal system, and its mechanical stability is determined according to the following formula (applied to Laue class 4/ mmm) [25]:

$$\begin{aligned} C_{11} > |C_{12}|, 2C_{13}^2 < C_{33}(C_{11} + C_{12}) \\ C_{44} > 0, C_{66} > 0 \end{aligned} \quad (2)$$

From Table 2, it can be concluded that both the M1 and M2 phase is mechanically stable as the independent elastic constants of M1 and M2 are all positive and satisfy the above criteria. It can also be

found that the C_{11} values of the M1 and M2 phase are much smaller than those of the $(\theta, \theta', \Omega)$ - Al_2Cu phases, indicating that M1 and M2 are much easier to compress along the $[100]$ directions.

In order to investigate the dynamical stability of the proposed M1 and M2 phases, their phonon dispersions were calculated by the finite displacement method, as shown in the Figure 5b. We can clearly see that there are no imaginary frequencies in the phonon spectrum, suggesting both M1 and M2 phases are dynamically stable. As all Al_2Cu phases studied in the present work could be considered to be a special solution of the pseudo Al_2Cu phase and the $(\theta, \theta', \Omega)$ - Al_2Cu phases have been observed, it is reasonable to expect that the proposed M1 and M2 phases might also be synthesized and observed under certain conditions like high-temperature or low-temperature, high-pressure, films, nanometer sized precipitates in aluminum alloys, etc.

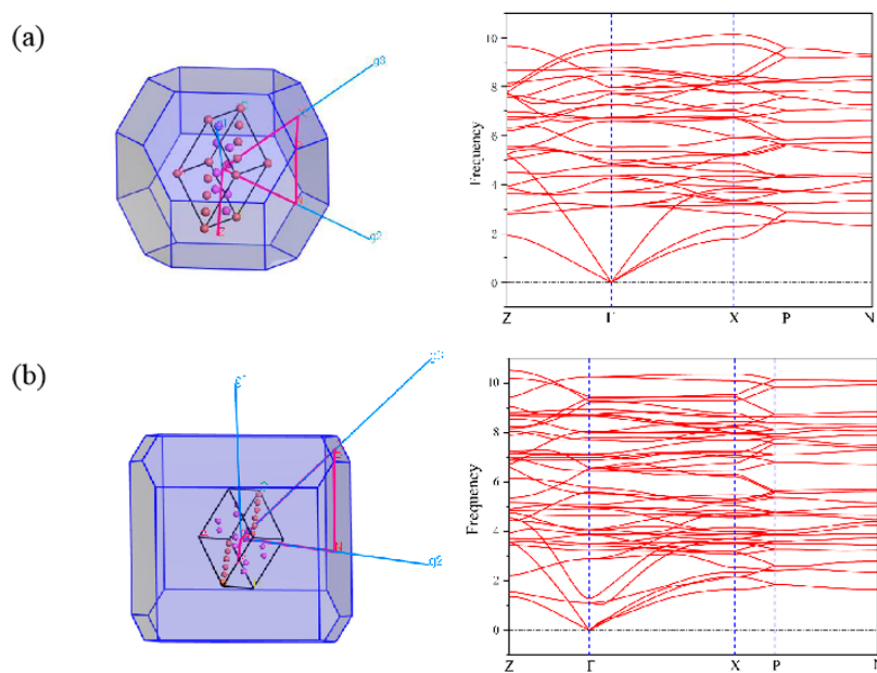


Figure 5. Brillouin zone diagram and phonon spectrum of (a) the M1 phase and (b) the M2 phase.

Considering the present assumptions might stimulate further experimental work, the electronic properties of the newly proposed M1 and M2 phases were also calculated including the band structure and density of states. As seen in Figure 6a,b, one can see that the energy band of both phases crossed the Fermi surface, indicating that they are still metallic. The density of states of both the M1 and M2 phases were quite similar, except that the density of states (DOS) at the Fermi level of the M2 was much higher than that of the M1 phase, as it contained more atoms. Their DOS could be divided into two regions—the one shown from -6 to -2 eV is mainly contributed by the Cu d states while the remaining region is mainly contributed by the Al s and p states.

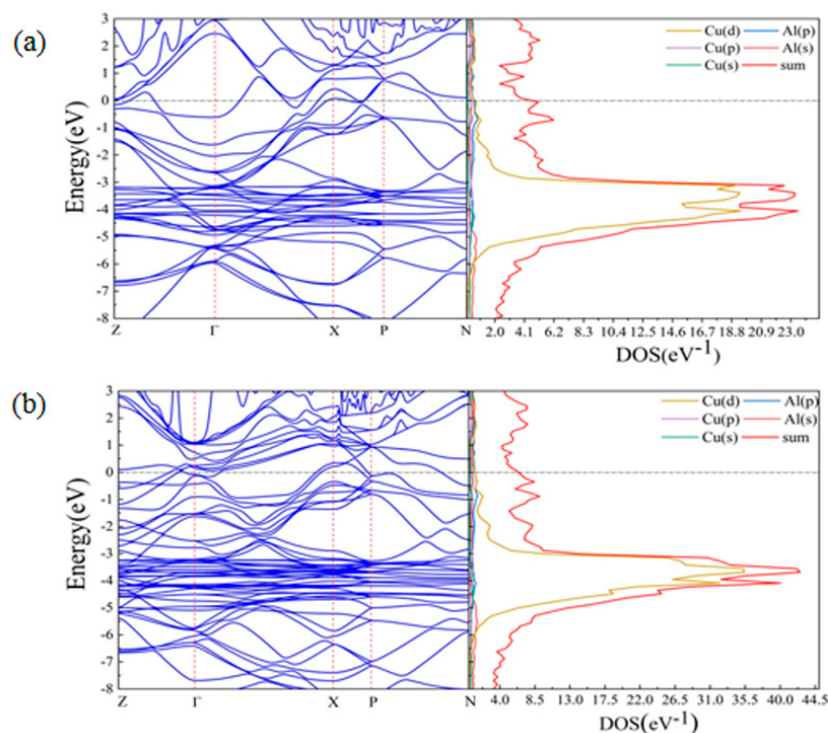


Figure 6. The electronic band structure and density of states of (a) the M1 phase and (b) the M2 phase.

4. Conclusions

In summary, we have clarified why the θ -Al₂Cu phase was incorrectly indexed and was refined to be the Owen phase during processing the single crystal X-ray diffraction datasets for twins of Al₂Cu sample. A pseudo Al₂Cu phase has been proposed while discriminating the diffraction information of two Al₂Cu phase single crystal domains, which could be considered as the average structure of the θ - and Ω -Al₂Cu phase, while the Owen phase could be considered to be the average structure of the pseudo Al₂Cu phase. It was confirmed that all existing Al₂Cu phases could be reconstructed by adjusting the packing sequences of two Al atomic net planes, encoded in the pseudo Al₂Cu phase. Furthermore, two potential Al₂Cu phases have been built-up by rearranging the packing sequences of the A/B layers of Al atoms. First-principles calculations showed that both phases are mechanically and dynamically stable. However, both phases are metastable according to the calculated enthalpy of formation values, implying that they can be observed only under certain favorable conditions like high-temperature or low-temperature, high-pressure, films, nanometer sized precipitates in aluminum alloys, etc. Band structures and density of states showed that both proposed phases are also metallic.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/9/10/1037/s1>, Figure S1: The structural model of the pseudo Al₂Cu phase, Figure S2: Projected simulated single crystal diffraction patterns of all existing and potential phases along [100], [010] and [001] directions, Table S1: Crystal data, data collection and structure refinement details of the pseudo Al₂Cu phase, Table S2: Crystallographic information of all existing Al₂Cu phases (the Owen-, θ -, θ' - and Ω phase) and two proposed potential Al₂Cu phases (M1 and M2 phase) corresponding to the available cif files.

Author Contributions: Conceptualization, C.F.; investigation, S.W. and C.F.; writing—original draft preparation S.W.; writing—review and editing, C.F.; project administration, C.F.; and funding acquisition, C.F.

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

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