Article

The Phase Stability of Al₃Er Studied by the First-Principles Calculations and Experimental Analysis

Chunlai Gao ¹, Kunyuan Gao ^{1,*}, Yusheng Ding ¹, Haonan Li ¹, Xiaolan Wu ¹, Shengping Wen ¹, Mu Gao ¹, Hui Huang ¹, Zuoren Nie ¹ and Dejing Zhou ²

¹ Faculty of Materials and Manufacturing, National Engineering Laboratory for Industrial Big-Data Application Technology, Beijing University of Technology, Pingleyuan 100, Chaoyang District, Beijing 100124, China; gclai@emails.bjut.edu.cn (C.G.); dingyusheng@emails.bjut.edu.cn (Y.D.); lihaonan1029@sjtu.edu.cn (H.L.); xiaolan.wu@bjut.edu.cn (X.W.); wensp@bjut.edu.cn (S.W.); gaomu@bjut.edu.cn (M.G.); huanghui@bjut.edu.cn (H.H.); znie@bjut.edu.cn (Z.N.)

² Yin Bang Clad Material Co. Ltd., Jiangsu Key Laboratory for Clad Materials, Wuxi 214145, China; dejing.zhou@cn-yinbang.com

* Correspondence: gaokunyu@bjut.edu.cn; Tel.: +86-10-6739-6439

Abstract: The thermodynamics of five Al₃Er compounds were investigated through first-principles density-functional theory (DFT) and experimental analysis. The Al₃Er compounds with Al₃Ho.hR20 (prototype Al₃Ho, Pearson symbol hR20), Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures exhibited formation energies of −0.412(−0.417), −0.411(−0.416), −0.400(−0.413), −0.399(−0.345) and −0.342(−0.345) meV/atom when using DFT with “standard” potential (“frozen core” potential) of Er. The results indicated that the Al₃Ho.hR20 structure was the thermodynamic stable phase and the other structures were metastable. The formation energy of Cu₃Au.cP4 structure was only 1 meV/atom less than that of Al₃Ho.hR20. Experimentally, the Al-30 wt.% Er alloys were cooled from 900 °C to 500 °C at the rate of 5 ± 2 °C/h and 60 ± 2 °C/h, respectively. The corresponding XRD analysis showed that the Al₃Ho.hR20 was formed at the cooling rate of 5 ± 2 °C/h and the Cu₃Au.cP4 was formed at the cooling rate of 60 ± 2 °C/h, which indicated that the Al₃Ho.hR20 was in a thermodynamic stable phase and the Cu₃Au.cP4 was in a metastable phase with high stability. The structural analysis indicated that the tiny energy difference between Al₃Ho.hR20 and Cu₃Au.cP4 might be attributed to a similar structure with varied stacking sequences.

Keywords: Al₃Er; phase stability; first-principles

Citation: Gao, C.; Gao, K.; Ding, Y.; Li, H.; Wu, X.; Wen, S.; Gao, M.; Huang, H.; Nie, Z.; Zhou, D. The Phase Stability of Al₃Er Studied by the First-Principles Calculations and Experimental Analysis. *Metals* **2021**, *11*, 759. <https://doi.org/10.3390/met11050759>

Academic Editor: Imre Bakonyi

Received: 10 March 2021

Accepted: 2 May 2021

Published: 4 May 2021

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1. Introduction

Micro-alloying is one of the efficient approaches utilized to improve strength and to increase the recrystallization temperature of aluminum alloys. By adding several transition or rare-earth elements, nanoscale coherent stable Cu₃Au.cP4 structure Al₃M particles can precipitate in aluminum alloys from supersaturated aluminum solid-solution, resulting in an increase in strength and the recrystallization temperature [1–3]. Sc is the most widely studied micro-alloying element, because the Cu₃Au.cP4 structure Al₃Sc precipitated from supersaturated Al-Sc alloys could lead to a considerable increase of the strengthening in Al alloys [1]. However, the high cost of Sc inhibited the industrial application of Al-Sc alloys. Er was considered to be one of the potential substitutional elements, since Al₃Er with the same Cu₃Au.cP4 structure could precipitate during the heat treatment of Al-Er alloys [4–6].

The Al₃Er precipitates with Cu₃Au.cP4 structure was considered as the thermodynamic stable phase in the Al-Er binary phase diagram [7,8] or ternary system [9,10]. However, it was reported earlier [11] that, when the Al-20 wt.% Er alloy was cooled from 900 °C to 500 °C at the rate of 85 °C/h and 4 °C/h, the Al₃Er phase was found in Cu₃Au.cP4 and Al₃Ho.hR20 structure, respectively.

Theoretically, the stabilities of varied structures of Al₃Er were evaluated with different methods. A criteria was supposed by Vucht [12] that the thermodynamic stable Al₃M

(M = Lanthanide series rare earth) phases was determined by the radius ratio of Al/M. The stable phase of Al₃Er was determined to be of Cu₃Au.cP4 structure, and Al₃Er was actually located between Al₃Ho.hR20 and Cu₃Au.cP4 structure. Gao et al. [13] calculated the formation energies of Al₃Er phase in Al₃Ho.hR20, Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures at 0 K using first-principles with “frozen core” pseudopotentials. The pseudopotentials kept 11 4f electrons frozen in the core (“frozen core” potentials. FC) and Er was treated as 3-valence. The results showed that Al₃Er in hR20 structure was thermodynamically stable and Al₃Er in Cu₃Au.cP4, AlNd₃.hP8, Al₃Gd.hR12 and Ni₃Ti.hP16 structures were metastable. Mao et al. [14] calculated formation energies of Al₃Er in Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures, using the “frozen” potentials and taking the magnetic part into account. The results showed that Cu₃Au.cP4 structure was the most stable phase among those four structures. The two theoretical calculation results were not consistent with each other completely, due to whether the influence of 4f electrons is considered. For the “frozen core” potential of Er, 4f electron is not considered in the calculation, which can save on computational demand very well. However, for the “standard” potential of Er, 4f electron is considered, which may grant more accurate results.

In this paper, phase stability of the ground state of the intermetallic compound Al₃Er was investigated by both the first-principles calculation based on density functional theory and experimental method. The formation energies of Al₃Er compounds with Al₃Ho.hR20, Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures were evaluated, respectively, with “standard” potential and “frozen core” potential for Er. To access the zero-point energy of phonon contribution to the phase stability. We compute the phonon properties of Cu₃Au.cP4 and Al₃Ho.hR20 Al₃Er. To obtain the thermodynamically stable phase in experiment, hypereutectic composition Al-30 wt.% Er alloy was melted and solidified from 900 °C to 500 °C with cooling rates of 60 ± 2 °C/h and 5 ± 2 °C/h, respectively. The corresponding XRD was performed to identify the structure of the formed Al₃Er phase.

2. Computation and Experiment Method

2.1. Computation Theory

For the thermodynamic properties of a given defect-free nonmagnetic material system at temperature *T* (in Kelvin) and volume *V*, within DFT, we can decompose the Helmholtz free energy as follows [15]:

$$F(V, T) = E_{0K}(V) + F^{el}(V, T) + F^{qh}(V, T) + F^{ph-ph}(V, T) + F^{el-ph}(V, T) \quad (1)$$

In the ab initio frame, $E_{0K}(V)$ was the ground state energy at 0 K, $F^{el}(V, T)$ came from electronic free energy. $F^{qh}(V, T)$, $F^{ph-ph}(V, T)$ and $F^{el-ph}(V, T)$ were the quasi-harmonic, anharmonic and electron-phonon coupling free energy [15,16]. For solid systems, the contribution from electronic, pressure, volume, anharmonic approximation was a smaller magnitude of order than that of the ground state energy [15], which would be neglected in computing formation energies. In the harmonic approximation, zero-point energy (ZPE) may affect the stability calculations, cannot be neglected. Based on the above analysis, the relative phase stability properties of a binary compound was in comparison with the formation enthalpy difference which contained ground state energy and ZPE between compounds with different structure and the same composition [17–22]. The compound and its constituents in their equilibrium crystal structures were at 0 K. Therefore, the formation enthalpy (eV/atom) of Al₃Er compounds could be calculated as:

$$\Delta H_{ord}^{eq}(Al_3Er) = E_{Al_3Er} - \left[\frac{3}{4} E^{eq}(Al) - \frac{1}{4} E^{eq}(Er) \right] \quad (2)$$

where the $H_{ord}^{eq}(Al_3Er)$, $E^{eq}(Al)$ and $E^{eq}(Er)$ are the sum of ground state energies and ZPE (per atom) of the compound Al₃Er and constituents, after Al and Er were relaxed to their

equilibrium and zero-pressure geometries, respectively, and 3/4, 1/4 were the composition of Al and Er in the compound.

2.2. Computational Details

The first-principles calculations were based on DFT and with projector-augmented plane-wave (PAW) method [23] as implemented in Vienna ab initio simulation package (VASP, version 5.3) [24,25]. The exchange-correlation energy function used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [26,27]. In the calculations, all structures were fully relaxed with respect to the cell lattice vector and inner atomic coordinates by minimizing the total energy until less than 1 meV. The convergence of energy with respect to the energy cutoff and k-mesh point were tested carefully. A plane-wave basis set was set as 360 eV, a $0.13 \text{ \AA}^{-1}$ spacing Monkhorst-Pack [28,29] k-mesh was used in the integration over the Brillouin zone for all calculations. Unless otherwise specified, for relaxations, the reciprocal space energy integration was performed by 1-ordered Methfessel-Paxton [30] technique with sigma of 0.05 eV. For the final static calculations of total energies, the tetrahedron method was used, corrected by Blöchl [31]. In the relax calculations, all the atomic configuration was assumed to be converged when the Hellman-Feynman forces were smaller than $0.0001 \text{ eV/\AA}$. In the relax calculation and static calculations, the total energy was converged within 10^{-6} eV .

Er and its trialuminide displayed ferromagnetism or antiferromagnetic at lower temperatures and paramagnetism at temperature above 300 K [32,33]. Therefore, it could be treated as paramagnetism in calculations. In the present VASP's pseudopotentials dictionary, there were three types of potentials for the Er element. The first one included the partial 4f electrons within the core level and its valence was 2, valence state $5p^6 6s^2$ for Er. The second pseudopotential for Er with 4f-electrons in the core level and its valence was 3+ (so-called "frozen core" potential), whose valence state was $5p^6 5d^1 6s^2$. The third potential treated Er as 3+, whose valence state was $4f^{11} 5s^2 5p^6 5d^1 6s^2$ (so-called "standard" potential. ST) treated all the 4f electrons in the valence band.

Because some experiments and theory confirmed the 4f and 5d electrons could be hybridized for Er, partial 4f electrons could form bonds with other elements [34–38]. Usually, Er was treated as 3+ in calculations, instead of 2+ [13,38]. Therefore, treating Er as valence of 2 could not assess the 4f effect on structure's calculation and thermal properties accurately. For the FC potential, treating Er as 3+ could save computational demanding very well, in approximation to the out-valence electron distribution, which was applied in many calculations [13,14,39,40]. The electron distribution of ST potential close to the real 4f-electron distribution in the Er element could assess the 4f-electron effect on thermodynamic property calculations, accurately. In this study, in order to illustrate whether the f-electrons affected thermodynamic phase stability of Al_3Er phase, both the "standard" and "frozen core" potential were used.

In this work, the phonon contribution at zero point was also predicted by using the Phonopy [41] simulation package based on the second (harmonic) force constants. The harmonic force constant is calculated using the direct approach base on the finite displacement method. We tested the convergence of the harmonic force constant with a $3 \times 3 \times 3$ supercell of Al, Er and $\text{Cu}_3\text{Au.cP4 Al}_3\text{Er}$ primitive cell, $2 \times 2 \times 2$ supercell of $\text{Al}_3\text{Ho.hR20 Al}_3\text{Er}$ primitive cell, to ensure the convergency of the results. In the ZPE calculation, we found a relative shift (0.25, 0.25, 0.25) with respect to the Γ point, and an interpolation mesh of $30 \times 30 \times 30$ grids points of Al, $\text{Cu}_3\text{Au.cP4 Al}_3\text{Er}$, $36 \times 36 \times 27$ grids points of Er, $35 \times 35 \times 30$ grids points of $\text{Al}_3\text{Ho.hR20 Al}_3\text{Er}$, the ZPE was valid down to 0.05 meV/atom . Because the self-consistent calculation of supercell—while using the ST potential—could not be achieved, we used the FC potential for Er elements. Furthermore, configurational effects, which may arise from defects in the structure, could stabilize the structures when the temperature is not zero. Experimentally, $\text{Cu}_3\text{Au.cP4}$ structure Al_3Er was a common precipitate in aluminum alloy, but its microstructure has not been observed as bulk material. For $\text{Al}_3\text{Ho.hR20}$ structure Al_3Er , its microstructure has not been studied

so far. In this study, we didn't consider configurational effects in the calculation process for simplification. Thereafter we would carry out the solidification experiments on Al-30 wt.% Er alloy with different cooling rates to ascertain the thermodynamically stable phase. For the details, see below.

2.3. Experimental Method

The alloys with nominal composition of Al-30 wt.% Er were brought from Hunan Rare Earth Metal Materials Research Institute. Its composition was measured to be Al-29.45 wt.% Er by X-ray fluorescence measurement. They were firstly cut into blocks and put into an alumina crucible with a diameter of 25 mm. Then they were sealed in quartz tube protected by argon gas with a vacuum of 10^{-3} Pa. The specimens were heated to 1000 °C and kept for 60 min, then cooled to 900 °C above the liquidus [7,8], and then to 500 °C below the eutectic temperature [7,8] at the cooling rate of 60 ± 2 and 5 ± 2 °C/h, respectively. The cooling rate curves are indicated in Figure 1.

Figure 1. Scheme of heat treatment of Al-30 wt.% Er, cooling rate of 60 ± 2 °C/h and 5 ± 2 °C/h, respectively.

The structures of the samples with two different cooling rates were analyzed using X-ray diffractometry (XRD D8 advance, Bruker, Karlsruhe, Germany) with Cu K α radiation with wavelength of 1.5406 Å, current of 30 mA and voltage of 35 kV. The scanning speed was 4 degrees/min.

3. Results

3.1. Computational Results

Since the Al₃Er precipitates were observed in the structure of Cu₃Au.cP4 and Al₃Ho.hR20 structures experimentally [12,42,43], and the corresponding lattice parameters were measured, we firstly verified two kinds of potential of Er by comparing the experimental value of lattice parameters with calculated ones by relaxation of Al₃Er with these two structures. The relaxed lattice constants using treating the 4f-electrons in the core band ("frozen core" potential) or valence band ("standard" potential, ST) were listed in Table 1. For Cu₃Au.cP4 structure, the calculated lattice constants were 4.238 Å and 4.215 Å by using "frozen core" and "standard" potential, respectively. As listed in Table 1, the lattice parameter of Al₃Er with Cu₃Au.cP4 structure was 4.215 Å [12], 4.212 ± 0.002 Å [42] and 4.214 Å [43] from several reports. Table 1 also presents detailed comparisons between calculations and experimental results of lattice constants. We found that the difference between the calculation results of lattice constants at 0 K and the experimental result at ambient temperature is within 1%, which indicates that the lattice constants calculated by both frozen core potential of Er and standard potential of Er were acceptable.

Table 1. The calculated and experimental lattice constants of Al₃Er in Cu₃Au.cP4 and Al₃Ho.hR20 structures with different potentials.

Structure	Lattice Constants/ Å			Difference/%	
	ST	FC	EXP	ST	FT
Cu ₃ Au.cP4	4.215	4.238	4.215 [12]	0.0	0.5
			4.212 ± 0.002 [42]	0.1	0.6
			4.214 [43]	0.0	0.6
Al ₃ Ho.hR20	5.993	6.063	6.025 [12]	−0.5	0.6
	5.993	6.063	6.025 [12]		
	36.059	35.820	35.675 [12]	1.1	0.4

Based on the verification of the Er potential, relaxation of the AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures were performed by using “standard” potential and “frozen core” potential. After relaxation calculation on each structure, static calculations were performed to get the formation energy. The main results of formation energy and relative energy by using different potentials of this paper were summarized in Table 2.

Table 2. The formation energy and other properties of Al₃Er in different structures with different potentials.

Structure	Formation Energy with ST	Formation Energy with FC	Relative Energy		Ref.
			ST	FC	
			eV/atom		
Al ₃ Ho.hR20	−0.412	−0.417 * −0.412 **	0	0 * 0 **	
Cu ₃ Au.cP4	−0.411	−0.416 * −0.404 **	0.001	0.001 * 0.008 **	−0.416 [13] −0.416 [39] −0.417 [44]
Al ₃ Gd.hR12	−0.400	−0.413 *	0.012	0.004 *	
AlNd ₃ .hP8	−0.399	−0.345 *	0.013	0.072 *	
Ni ₃ Ti.hP16	−0.342	−0.345 *	0.060	0.072 *	

* without ZPE correction. ** with ZPE correction.

From Table 2, it was clearly seen that the formation energy of Al₃Er with Al₃Ho.hR20 structure of −0.412 eV/atom and/or −0.417 eV/atom was the lowest formation energy, indicating that the Al₃Ho.hR20 structure was the thermodynamic stable phase. Also, the formation energies of Al₃Ho.hR20 structure by using different potential were set to zero. Then the relative energies of other four structures compared with the formation energy of Al₃Ho.hR20 were listed in the fourth and fifth columns of Table 2. It could be found that the formation energy differences of Cu₃Au.cP4, Al₃Gd.hR12 and AlNd₃.hP8 were less than the room temperature thermal energy ($k_B T = 26$ meV/atom) [13], suggesting that all of them were thermodynamically metastable. Especially among all the metastable phases, Cu₃Au.cP4 structure was of the lowest formation energy, only 1 meV/atom above the Al₃Ho.hR20, indicating the most energetically favorable metastable phase. This result was in agreement with the results proposed by Gao et al. [13]. In Table 2, we also show the calculation results of Al₃Ho.hR20 and Cu₃Au.cP4 Al₃Er when ZPE correction was considered. The difference of formation energy between the Al₃Ho.hR20 and Cu₃Au.cP4 Al₃Er changed from 0.001 eV/atom to 0.008 eV/atom, which became larger. Although the difference is still small, the results did show that Al₃Ho.hR20 was the thermodynamically stable structure of Al₃Er. The relative formation energies of Al₃Gd.hR12 were 12 and 4 meV/atom with “standard” potential and “frozen core” potential, lower than one half of the room temperature thermal energy, which implied that the Al₃Gd.hR12 was in an energetically favorable metastable phase. For the AlNd₃.hP8 and Ni₃Ti.hP16 structure, by “frozen core” potential, both structures have the same formation energy of

72 meV/atom. However, by the “standard” potential, the formation energy of $\text{AlNd}_3\text{.hP8}$ was 13 meV/atom, the formation energy of $\text{Ni}_3\text{Ti.hP16}$ was 60 meV/atom. Thus, it was shown that the “standard” potential did not lead to a different sequence of the relative stability but did affect the values of relative formation energies.

3.2. Experimental Results

Hypereutectic alloy was selected with the composition of Al-30 wt.% Er, and the Al_3Er phase was formed from the liquid directly. After solidification with the cooling rate of $60 \pm 2^\circ\text{C}$ and $5 \pm 2^\circ\text{C/h}$ from 900°C to 500°C , the alloy was analyzed by XRD and the results were shown in Figure 2. Figure 2a was the XRD spectrum of the sample formed with a cooling rate of $60 \pm 2^\circ\text{C/h}$. It could be found that the peaks were from the $\text{Cu}_3\text{Au.cP4}$ type Al_3Er and FCC Al. Figure 2b shows the XRD spectrum of the sample formed with a cooling rate of $5 \pm 2^\circ\text{C/h}$. The peaks were from the $\text{Al}_3\text{Ho.hR20}$ structure Al_3Er and FCC Al.

Figure 2. XRD spectrum of Al-30 wt.% Er for cooling rate of (a) $60 \pm 2^\circ\text{C/h}$ and (b) $5 \pm 2^\circ\text{C/h}$, respectively.

The results indicated that the $\text{Cu}_3\text{Au.cP4}$ structure Al_3Er formed in the alloy with a higher cooling rate of $60 \pm 2^\circ\text{C/h}$, while the $\text{Al}_3\text{Ho.hR20}$ -structured Al_3Er formed with a lower cooling rate of $5 \pm 2^\circ\text{C/h}$. The only difference between these two processes was the cooling rate, and the latter was closer to an equilibrium state. Hence, the $\text{Al}_3\text{Ho.hR20}$ was the thermodynamically stable structure, and $\text{Cu}_3\text{Au.cP4}$ was the very stable metastable structure.

4. Discussion

From the above formation energy calculation results, Al_3Er with five crystal structures were of close negative values, indicating large thermodynamic trends for formation of all the five structures. Among them, $\text{Al}_3\text{Ho.hR20}$ structure was of the most negative formation energy, and $\text{Cu}_3\text{Au.cP4}$ was of only 1 meV less value. The thermodynamic stable phase with $\text{Al}_3\text{Ho.hR20}$ structure was confirmed by solidification of Al-30 wt.% Er alloy with the very low cooling rate of $5 \pm 2^\circ\text{C/h}$, and the metastable phase with $\text{Cu}_3\text{Au.cP4}$ structure was easily formed with higher cooling rate of $60 \pm 2^\circ\text{C/h}$.

The very small difference in formation energy between $\text{Al}_3\text{Ho.hR20}$ and $\text{Cu}_3\text{Au.cP4}$ structure could be discussed from the point view of the crystal structure. Both structures could be constructed by stacking the close-packed planes but with different sequences, as shown in Figure 3. In Figure 3a, we show the side view of $\{1\bar{1}0\}$ plane with an atom in the plane passing through the (0,0,0) (large size) and (0.5,0,0.5) point (small size), normal to the $\{111\}$ plane of $\text{Cu}_3\text{Au.cP4}$ Al_3Er . In Figure 3b, we show the $\{1\bar{1}00\}$ plane with atom in the plane passing through the (0,0,0) (large size) and (0.5,0.5,0) point (small size), normal to the $\{11\bar{2}0\}$ plane of $\text{Al}_3\text{Ho.hR20}$ Al_3Er . From Figure 3, it can be seen that the stacking sequence of $\text{Cu}_3\text{Au.cP4}$ was 3-layer ABC, while that of the $\text{Al}_3\text{Ho.hR20}$ structure was a 15-layer ABCBCBCACACABAB. The similar structure with only varied stacking sequence could lead to a tiny formation energy difference between these two structures.

Figure 3. Side view of the stacking sequences for Al_3Er with (a) $\text{Cu}_3\text{Au.cP4}$ and (b) $\text{Al}_3\text{Ho.hR20}$ structure.

5. Conclusions

The formation energies of $\text{Al}_3\text{Ho.hR20}$, $\text{Cu}_3\text{Au.cP4}$, AlNd3.hP8 , $\text{Ni}_3\text{Ti.hP16}$ and $\text{Al}_3\text{Gd.hR12}$ structures at 0 K were calculated based on first principles using “Standard” potential and “frozen core” potential for Er. When taking the vibrational effect into account with ZPE correction, the difference of formation energy between the $\text{Al}_3\text{Ho.hR20}$ and $\text{Cu}_3\text{Au.cP4}$ structure Al_3Er was changed from tiny 0.001 eV/atom to 0.008 eV/atom, indicating that Al_3Er with $\text{Al}_3\text{Ho.hR20}$ structure was thermodynamically stable phase, while that with $\text{Cu}_3\text{Au.cP4}$ structure was the most stable metastable phase.

Experimentally, the solidification of Al-30 wt.% Er alloy showed that the $\text{Cu}_3\text{Au.cP4}$ structure Al_3Er formed in the alloy with a cooling rate of 60 ± 2 °C/h, while the $\text{Al}_3\text{Ho.hR20}$ -structured Al_3Er formed with very low cooling rate of 5 ± 2 °C/h, which proved that the thermodynamic stable phase was a $\text{Al}_3\text{Ho.hR20}$ structure, in good agreement with the theoretical calculation result.

Author Contributions: Conceptualization, K.G. and Z.N.; methodology, K.G.; validation, C.G., Y.D. and H.L.; formal analysis, K.G.; investigation, C.G., H.L., X.W., S.W., M.G. and H.H.; resources, K.G.; data curation, K.G.; writing—original draft preparation, C.G.; writing—review and editing, K.G.; supervision, Z.N.; project administration, K.G., D.Z. and Z.N.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (51671005, 51621003 and 51701006) and Beijing Natural Science Foundation (2202009), Basic Research Program of Jiangsu Province (Natural Science Foundation) (BK20181143 and BK20191148) and International cooperation project in Jiangsu Province (BZ2019002).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data generated/analyzed are included in this manuscript. Correspondence and requests for the raw data and materials should be addressed to G.C. (gclai@emails.bjut.edu.cn) and the corresponding author G.K.

Acknowledgments: We would like to thank Jianbo Liu, Sixten Boeck and Baisheng Sa for fruitful discussions.

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

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