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Cu-deficiency Induced Structural Transition of $Cu_{2-x}Te$

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Abstract

The crystal structure of the binary compound Cu_2Te had not been well-determined after decades of study. The hexagonal Nowotny structure was proposed in 1946, however, recent calculations showed that a new monoclinic structure and a trigonal one have much lower energies. Using first-principles calculations, we show that all the reported structures of Cu_2Te are metastable with respect to the phase separation $Cu_2Te \rightarrow Cu_{2-x}Te + xCu$, i.e., the Cu vacancies (Cu deficiency) can form spontaneously in Cu_2Te. The formation of Cu vacancies causes a structural transition of $Cu_{2-x}Te$ from the monoclinic (most stable when $x=0$), to trigonal ($0.125 \le x \le 0.625$), and then to hexagonal Nowotny structure ($0.75 \le x < 1$). The X-ray diffraction (XRD) spectra of these structures are simulated, showing that the experimental XRD peaks of four different $Cu_{2-x}Te$ samples can be attributed to the trigonal structure. Based on this, we predict that the synthesized $Cu_{2-x}Te$ samples (Weissite mineral) with $0.125 \le x \le 0.625$ should crystallize mainly in the trigonal, rather than in the previously-recognized hexagonal Nowotny structure. The lattice constants and atomic coordinates of different structures are calculated, which can be used in the future refinement of the $Cu_{2-x}Te$ XRD spectra. Our study shows that the Cu-deficiency-induced structural transition should be considered in the study and application of $Cu_{2-x}Te$ compounds.

Keywords: $Cu_{2-x}Te$, Cu chalcogenides, structural transition, Cu vacancies, first-principles calculation.

I. Introduction

Ternary and quaternary Cu chalcogenides such as $CuInSe_2$, $CuGaSe_2$, Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ are all very promising photovoltaic semiconductors for thin-film solar cells, and thus have attracted intensive attention during the past decades[1-3]. As their binary counterpart, the Cu chalcogenides such as Cu_2S, Cu_2Se and Cu_2Te have also been proposed as functional materials in solar cells[4-7], as well as in nonvolatile memory, photodetectors[8], batteries[9], thermoelectric[10,11] and biomedical devices[12]. However, the device performance so far is less satisfactory. One important reason is that many fundamental properties of Cu_2S, Cu_2Se and Cu_2Te are not clear, e.g., the most fundamental crystal structures of these binary compounds have not been well determined[13-15]. Until very recently there are still new findings in their crystal structures: (i) the previously proposed structure for high chalcocite Cu_2S was found incorrect[16], (ii) new low-energy structures were found for both Cu_2Se and Cu_2Te[13]. For Cu_2Te, a hexagonal structure was proposed in 1946, which was named the Nowotny structure in the following decades[17]. However, in 2007 Da Silva *et al.* found that the trigonal structure has lower energy than the Nowotny structure[18], and in 2012 Nguyen *et al.* discovered a new monoclinic structure through a global structural search[13], which has even lower energy than both the trigonal and Nowotny structures. Since the crystal structure is not clear, the study on other material properties becomes controversial.

The experimental determination of the Cu_2Te (also Cu_2S and Cu_2Se) crystal structures is limited by the commonly observed Cu-deficiency, which makes the synthesized samples usually non-stoichiometric, e.g., the Cu-deficient $Cu_{2-x}Te$ samples have x varying from 0 to 1[4,9,11,19-21]. The structures of non-stoichiometric samples may differ from that of the stoichiometric Cu_2Te, so the structure determination becomes more complicated. Since the monoclinic and trigonal structures are energetically more favorable, they should be dominant in the Cu_2Te samples at low temperature. However, previous experiments reported only the hexagonal Nowotny structure with the lattice constants and atomic coordinates determined[13,15,17], whereas the new monoclinic or trigonal structures have not been observed despite that their energies are lower[13,18]. The reason so far is not clear. One possible explanation is that the synthesized samples are non-stoichiometric ($x\neq0$), so the structure may differ from the stable one at $x=0$. This, however, is just an assumption. It is still an open question how the crystal structure of $Cu_{2-x}Te$ depends on the degree of the Cu-deficiency (the parameter x).

In this work, starting from four low-energy Cu_2Te structures, we studied the formation of Cu vacancies (Cu-deficiency) using a first-principles calculation. We found that the formation of Cu vacancies in Cu_2Te is thermodynamically spontaneous, causing the phase separation of Cu_2Te into $Cu_{2-x}Te+xCu$. When Cu vacancies are formed, the most stable structure changes from the monoclinic (most stable when x=0), to trigonal ($0.125\leq x\leq 0.625$), and then to hexagonal Nowotny structure ($0.75\leq x<1$). The simulated X-ray diffraction (XRD) peaks of the trigonal structure have good agreement with the published experimental spectra of $Cu_{2-x}Te$, such as the standard peaks in the JCPDS (Joint Committee on Powder Diffraction Standards) database. Instead, the XRD peaks of the relaxed Nowotny structure do not agree with the experimental ones. On this ground, we predict that the synthesized $Cu_{2-x}Te$ samples with x=0.125-0.625 should crystallize mainly in the trigonal, rather than in the previously recognized hexagonal Nowotny structure.

II. Structure Models and Calculation Methods

As shown in Fig. 1, four structures of stoichiometric Cu_2Te are considered in the current study. The first is the hexagonal Nowotny structure, whose lattice constants and atomic coordinates were given in the experimental literature[15,17]. The second is the monoclinic structure that was identified recently from the global search and has the lowest energy among all structures[13]. The third and fourth are the trigonal and tetragonal structures respectively[18]. They are constructed based on the experimentally proposed structures of non-stoichiometric $Cu_{1.75}Te$ (trigonal[22,23]) and $Cu_{1.5}Te$ (tetragonal Rickardite)[24,25], in which some of the Cu sites are partially occupied. Through occupying all the Cu sites, we can construct trigonal and tetragonal Cu_2Te structures. In Table I, their space group, lattice constants and atomic coordinates are listed.

Comparing the four Cu_2Te structures, we can see that they are all layered structures, with the Cu cations in the middle of layers and the Te anions (in Nowotny and monoclinic structures) or both the Cu cations and Te anions (in trigonal and tetragonal structures) terminating the layers. The distance between layers is more than 2.8 Å, and the distances between atoms in different layers are even larger, more than 3.5 Å. From the top view of these structures (bottom part of Fig. 1), we can also find that the Te anions on the surface of Cu_2Te layers are all hexagonally coordinated by Cu cations in the hexagonal Nowotny, monoclinic and the trigonal structures. In the Nowotny structure the hexagonal lattice is ideal, whereas in the monoclinic and trigonal structures they are slightly stretched. In contrast with others, the tetragonal structure has the surface Te anions coordinated by 4 Cu cations as the first-nearest-neighbors and by 4 more Cu cations as the second-nearest-neighbors.

The Cu-deficient $Cu_{2-x}Te$ structures are constructed by building up 24-atom supercells of the four Cu_2Te structures, and then removing certain Cu atoms. When one Cu atom is removed (corresponding to x=0.125, $Cu_{1.875}Te$), there are at most 16 possible structure configurations. We calculate the total energy of all the configurations and determine the lowest-energy configuration, from which we remove one more Cu atom and determine the lowest-energy configuration for x=0.25

($Cu_{1.75}Te$). This process is repeated until 8 Cu atoms are removed (x=1, i.e., CuTe).

With the structures constructed for $Cu_{2-x}Te$, we studied their stability using the total energy calculations based on the density functional theory (DFT) as implemented in the VASP code[26]. The kinetic energy cutoff for the plane-wave basis is set to 500 eV. A 4×4×4 or equivalent k-point mesh is used for the 24-atom supercells. The Perdew-Burke-Ernzerhof (PBE)[27] exchange-correlation functional was employed, and the effect of van der Waals interaction is included within the van der Waals density functional (VDW-DF)[28,29] scheme because of the layering of all the structures. All the lattice constants and atomic coordinates are relaxed through minimizing the stress and force.

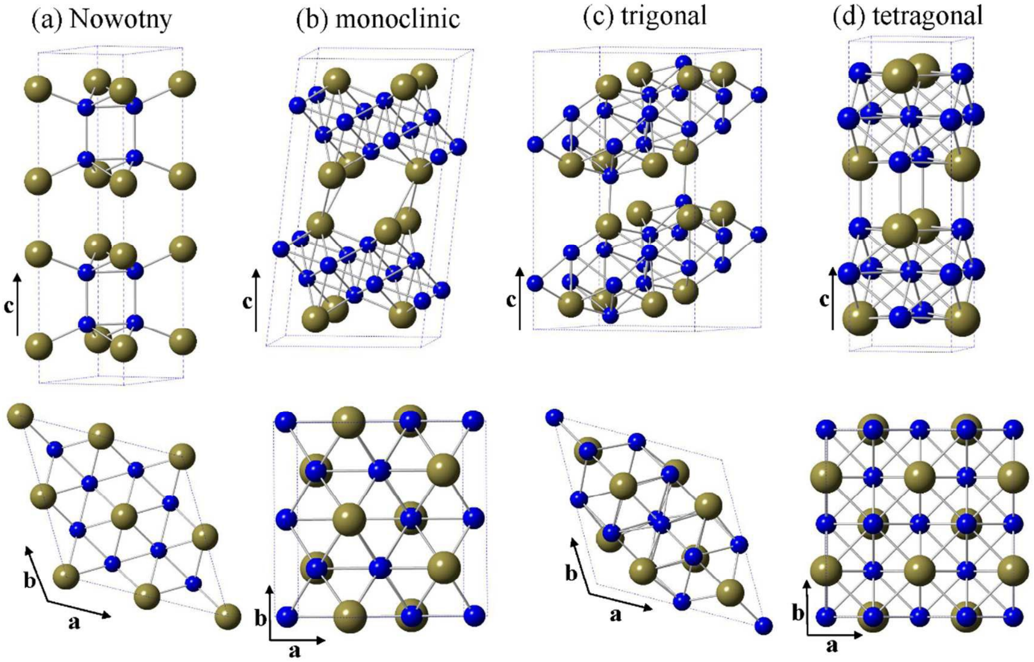

Figure 1. Crystal structures of (a) hexagonal Nowotny, (b) monoclinic, (c) trigonal, and (d) tetragonal structures of Cu_2Te. The yellow and blue spheres show the Te and Cu atoms, respectively. Both the side view (top) and the top view (bottom) are shown.

Table I. Structural information (space group, lattice parameters and atomic coordinates) of the four Cu_2Te structures.

Structure	Space group	Lattice parameters	Atomic coordinates
Nowotny	P6/mmm, No. 191	a=b=4.26 Å, c=8.11 Å α=β=90°, γ=120°	Cu (0.33,0.67,0.34) Te (0.00,0.00,0.22)

Monoclinic	C2/m, No. 12	a=7.82 Å, b=3.88 Å, c=7.17 Å, α=γ=90°, β =98.1°	Cu (0.03, 0.00, 0.33) Cu (0.34, 0.00, 0.44) Te (0.70, 0.00, 0.19)
Trigonal	P-3m1, No. 164	a=b=8.37 Å, c=7.16 Å, α=β=90°, γ=120°	Cu (0.33,0.67,0.10) Cu (0.00,0.00,0.33) Cu (0.03,0.51,0.33) Cu (0.35,0.17,0.45) Te (0.15,0.30,0.21) Te (0.67,0.33,0.24)
Tetragonal	P4mm, No. 99	a=b=4.07 Å, c=6.03 Å, α=β=γ=90°	Cu (0.00,0.00,0.74) Cu (0.50,0.50,0.27) Cu (0.00,0.50,0.00) Te (0.50,0.50,0.71) Te (0.00,0.00,0.30)

III. Results and discussion

A. Formation of Cu vacancies in Cu_2Te and phase separation

For stoichiometric Cu_2Te, our calculated total energies of the monoclinic, trigonal, tetragonal and hexagonal Nowotny structures increase in order, which is consistent with the previous calculation by Nguyen *et al.* [13] Unexpectedly, the experimentally proposed Nowotny structure has a total energy not only higher than those of the monoclinic and trigonal ones (by 0.53 and 0.44 eV/f.u. respectively), but also significantly higher than that of the tetragonal (by 0.34 eV/f.u.). The large energy difference indicates that the Nowotny structure has a very low possibility to exist in the synthesized stoichiometric Cu_2Te samples.

To predict whether the Cu vacancies will be formed in the Cu_2Te lattice, we calculate the formation energies of single or multiple Cu vacancies, which is defined as[3,30],

$$\Delta H(V_{Cu}) = \frac{E\left(Cu_{2-x}Te\right) + 8x*E(Cu) - E(Cu_2Te)}{8x} \qquad (1)$$

where $E(Cu_2Te)$ is the total energy of a 24-atom Cu_2Te supercell, $E(Cu_{2-x}Te)$ is the total energy of the same supercell but with 8x Cu vacancies (x shows the degree of Cu deficiency in the non-stoichiometric $Cu_{2-x}Te$), and E(Cu) is the total energy (per atom) of Cu metal in the face-centered-cubic structure. When there are multiple Cu vacancies in the supercell, $\Delta H(V_{Cu})$ is averaged to per Cu vacancy. For a certain x, a negative $\Delta H(V_{Cu})$ means that 8x Cu vacancies will be formed spontaneously among the 16 Cu sites in the 24-atom supercell, so Cu_2Te tends to have a phase separation into the non-stoichiometric $Cu_{2-x}Te$ and Cu metal.

The calculated $\Delta H(V_{Cu})$ are plotted in Fig. 2. Obviously, the values are different in the four structures, showing that the possibility for the formation of Cu vacancies depends on the specific crystal structures. The Nowotny structure has large and negative $\Delta H(V_{Cu})$, as large as -2.0 eV per vacancy when there are two vacancies among 16 Cu sites (x=0.25). This makes the phase separation from Cu_2Te to $Cu_{1.75}Te$+0.25Cu (or $Cu_{2-x}Te$+xCu) highly possible and spontaneous, so it should be very difficult to synthesize or stabilize stoichiometric Cu_2Te in Nowotny structure. The trigonal and tetragonal structures also have negative $\Delta H(V_{Cu})$ no matter for single or multiple Cu vacancies.

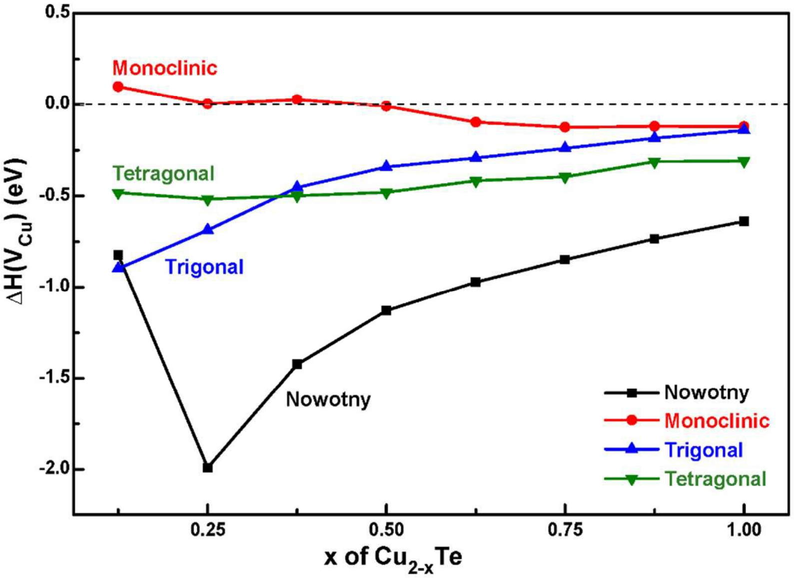

Figure 2. The calculated formation energy $\Delta H(V_{Cu})$ of Cu vacancies in monoclinic, Nowotny, trigonal and tetragonal Cu_2Te structures, as a function of the number of Cu vacancies in a 24-atom Cu_2Te supercell. x=0.125 means that one Cu vacancy is formed in the supercell, and x=1.0 means that eight Cu vacancies are formed. After the Cu vacancies are formed, the resultant composition of the supercell becomes $Cu_{2-x}Te$.

In contrast with the metastable structures, the most-stable monoclinic structure of Cu_2Te has a much smaller and even positive formation energies for Cu vacancies. When x<0.5 (less than 4 Cu vacancies are formed among the 16 Cu sites), $\Delta H(V_{Cu})$ is even positive, and only when 4 and more Cu vacancies are formed, $\Delta H(V_{Cu})$ becomes negative. The small values of $\Delta H(V_{Cu})$ indicate that the monoclinic Cu_2Te has a smaller tendency to form Cu vacancies and have a phase separation into $Cu_{2-x}Te$+xCu once the stoichiometric Cu_2Te samples are synthesized.

Since $\Delta H(V_{Cu})$ can be negative for all the four structures of Cu_2Te, they are metastable with respect to the phase-separation $Cu_2Te \rightarrow Cu_{2-x}Te + xCu$ from the thermodynamic point of view.

B. Structural transition of $Cu_{2-x}Te$

As discussed above, the formation energies of Cu vacancies in the metastable structures are much lower than those in the ground-state monoclinic structure, so the most stable structure of the non-stoichiometric $Cu_{2-x}Te$ may differ from that of the stoichiometric Cu_2Te, i.e., a structural transition may happen as the Cu-deficiency parameter x changes.

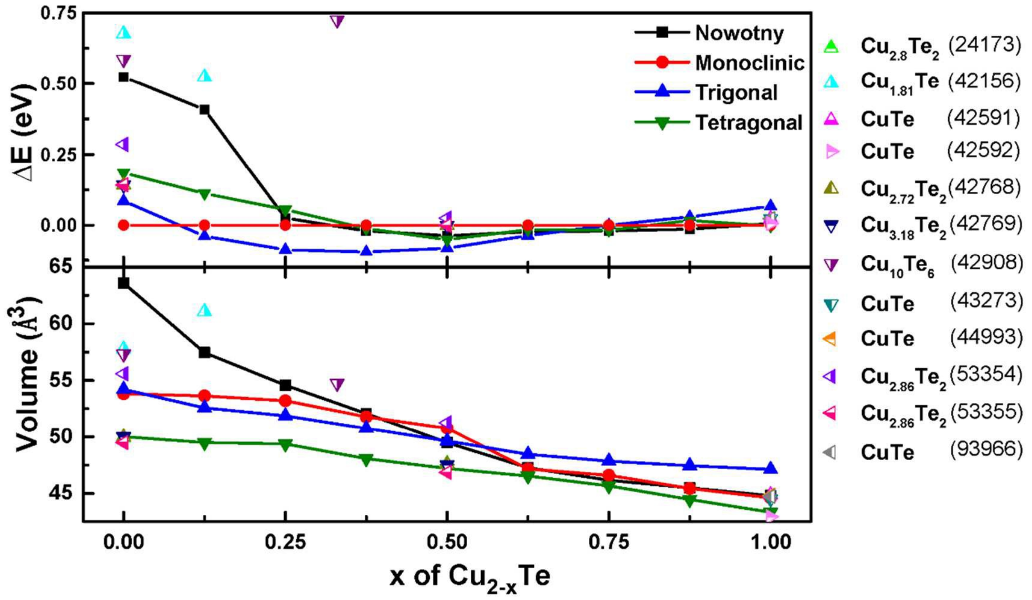

Figure 3. The calculated change of (a) the energy difference between the Nowotny (trigonal and tetragonal) and monoclinic structures, (b) the volume of $Cu_{2-x}Te$ in different structures as a function of x.

In Fig. 3(a), the energy difference ΔE between the three metastable structures and the monoclinic one is plotted as a function of x. At x=0, ΔE is positive for all the three structures, according to our expectation. As x increases ΔE decreases, and the value of the trigonal structure becomes negative at x=0.125, which means that the trigonal structure becomes the lowest-energy structure for $Cu_{1.875}Te$. As x increases from 0 to 1, the value of ΔE decreases first, and then approaches a minimum value at a certain x (0.375 for trigonal and 0.5 for Nowotny and tetragonal structures). At x=0.375, ΔE of Nowotny and tetragonal structures is also negative, showing that the three metastable structures become more stable than the monoclinic one. This can be understood considering that the three structures have large and negative formation energies for Cu vacancies. The values of ΔE increase at $x>0.5$, which can also be understood according to the change of $\Delta H(V_{Cu})$. As shown in Fig. 2, $\Delta H(V_{Cu})$ in the monoclinic structure is positive or zero at $x\leq0.5$, but becomes more and more negative at $x>0.5$, which decreases the energy of the monoclinic structure relative to other structures.

Fig. 3(a) shows clearly that the most stable structure of $Cu_{2-x}Te$ is the trigonal one for $0.125\leq x\leq0.625$, and changes to Nowotny or tetragonal for $0.75\leq x\leq1$. For $0.125<x<0.5$, the energy difference ΔE is large, indicating that the synthesized $Cu_{2-x}Te$ samples should crystallize mainly in the trigonal phase. However, for $0.625<x<1$ the energy difference ΔE is small, so it is possible that all the four phases coexist in the synthesized samples.

To understand the change in the relative stability of different structures, we plot the calculated volume of $Cu_{2-x}Te$ as a function of x in Fig. 3(b). Obviously the volumes of the tetragonal structures are always smaller than those of other structures, which results from the different coordination numbers of Te anions in the tetragonal structures, i.e., the Te anions in other structures are hexagonally coordinated by Cu cations while in the tetragonal structure they are not. For the Nowotny, trigonal and monoclinic structures, the change of volumes is in accordance with the change of energies. The volume of the trigonal structure is larger than that of the monoclinic structure at $x=0.0$, but decreases to a smaller value at $0.125\leq x\leq0.5$ and then increases to a larger value again at $x\geqslant0.625$. Similar trend can also be found in the change of energy, as shown in Fig. 3(a). Since the atomic coordination is similar in these structures, a smaller volume means shorter and stronger Cu-Te bonding, so the accordant change of the energies and volumes can be understood. It should be noted that other factors, such as the atomic coordination number and Madelung energy, also influence the relative stability of different structures, so the change of the energies and volumes is not exactly accordant.

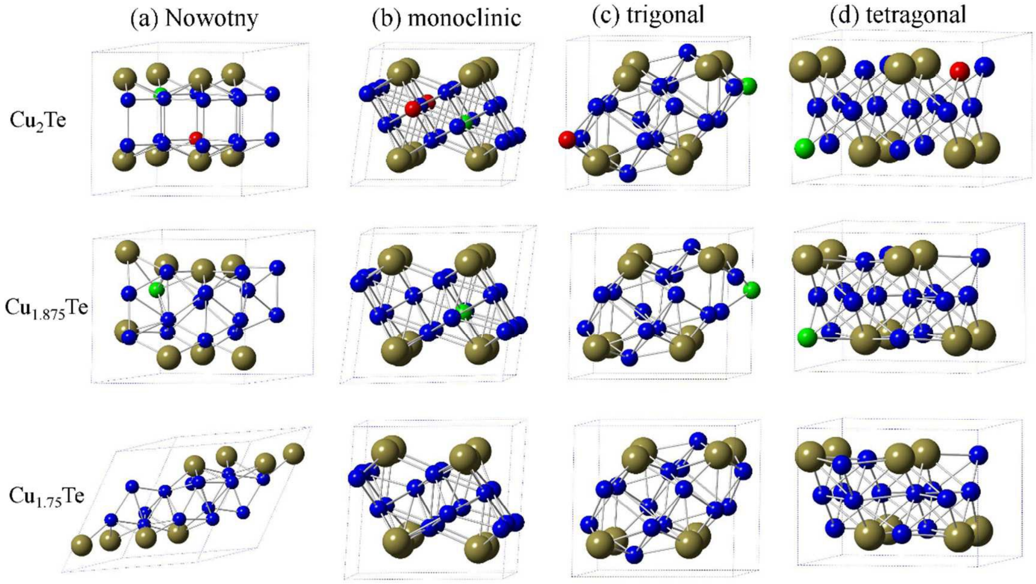

Figure 4. The structure distortion induced by the formation of Cu vacancies in the (a) Nowotny, (b) monoclinic, (c) trigonal and (d) tetragonal structures. From the top to the bottom, the structures of Cu_2Te, $Cu_{1.875}Te$ (with one Cu vacancy) and $Cu_{1.75}Te$ (with two Cu vacancies) are shown in order. The yellow and blue spheres show the Te and Cu atoms, respectively. The red (green) sphere shows the first (second) Cu atom that will be removed to form Cu vacancies.

The formation of Cu vacancies causes not only the change of the relative stability of different structures, but also their distortion. In Fig. 4, the structures of Cu_2Te, $Cu_{1.875}Te$ and $Cu_{1.75}Te$ are plotted. Dramatic distortion can be found for the Nowotny structures. Ideal Nowotny-Cu_2Te shows a high symmetry (space group No. 191), with two flat Cu sub-layers in the middle and two Te sub-layers on the surfaces. When one Cu atom is removed, the neighboring Te atom on the surface has an obvious displacement into the layer and the two flat Cu sub-layers disappear with the Cu atoms intermixed inside the $Cu_{1.875}Te$ layers. When two Cu atoms are removed ($Cu_{1.75}Te$), two Cu sub-layers appear again despite a large deformation of the supercell shape compared to that of ideal Cu_2Te. The dramatic distortion of the Nowotny structure explains the large negative formation energies of Cu vacancies (see Fig. 2), showing that the formation of Cu vacancies relaxes the structure significantly. The distortion in other structures is relatively smaller, i.e., the shape of the supercell is not deformed and there are only small displacements in the atomic coordinates.

In the discussion above, only four structures are considered for $Cu_{2-x}Te$, however, a search of the inorganic crystal structure database (ICSD) shows that at least 12 other structures have also been proposed for $Cu_{2-x}Te$ with x varying from 0 to 1. Some of them are supercell structures of those considered in the present study, but with Cu vacancies formed at different atomic sites. To see whether these $Cu_{2-x}Te$ structures are more stable than the most-stable structures that we have identified, we need to calculate their energies too. Unfortunately in most of these structures, the Cu sites are partially occupied, which makes the calculations of their energies very challenging. To compare their stability, we simplified the models and constructed 16 configurations for each structure with partial occupation (the composition x is chosen to be close to the experimental value). The calculated energy difference of 16 configurations is usually less than 0.1 eV/f.u., indicating that the partial occupation does not influence the stability significantly, so we picked up the lowest-energy configuration and plotted their energies by different triangles in Fig. 3. Through filling the Cu vacancies in these $Cu_{2-x}Te$ structures, the Cu_2Te structures are constructed and their energies are also plotted in Fig. 3. Interestingly the energies of these structures are always higher than the lowest-energy one among the trigonal, monoclinic, tetragonal and Nowotny structures, no matter at the experimental composition x or at x=0, so the predicted structural transition is not influenced by them.

C. X-ray diffraction patterns of $Cu_{2-x}Te$

As discussed above, our calculations show that there is a structural transition from the monoclinic structure at x=0 (Cu_2Te) to the trigonal one at $x \geq 0.125$ ($Cu_{1.875}Te$, $Cu_{1.75}Te$, etc.). Experimentally the x-ray diffraction (XRD) pattern of $Cu_{2-x}Te$ (known as Weissite mineral) is available in the JCPDS (Joint Committee on Powder Diffraction Standards) database with the power-diffraction-file (PDF) No. 10-1042, which was measured for $Cu_{1.81}Te$ (x=0.19). Recently the XRD spectra of different $Cu_{2-x}Te$ samples with x varying from 0 to 0.2 were also measured by a series of groups[4,31-34]. The availability of the experimental spectra makes it possible to compare the simulated XRD spectrum of our predicted structure with the experimental one, in order to figure out which structure exists in the synthesized $Cu_{2-x}Te$ samples.

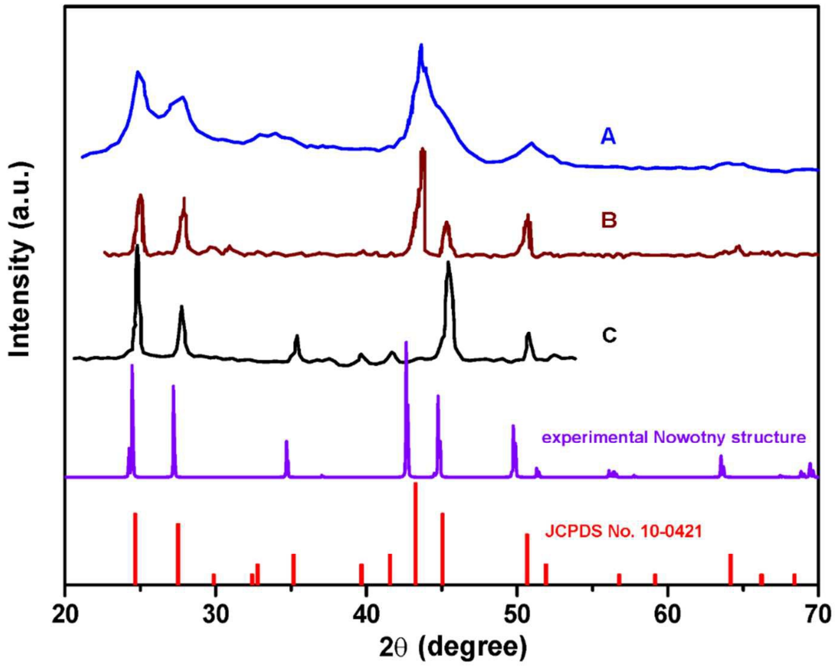

Figure 5. The experimental XRD spectra of $Cu_{2-x}Te$ samples synthesized by different groups: (A) $Cu_{2-x}Te$ nanocrystals[31], (B) $Cu_{1.93}Te$[32], (C) Cu_2Te thin films[33]. The red lines at the bottom show the standard XRD peaks taken from the JCPDS database for Weissite mineral ($Cu_{1.81}Te$, PDF No. 10-1042). The blue-violet line is the simulated spectrum of the Nowotny structure with the experimentally fitted lattice constants given in Ref. 15,17.

The experimental XRD spectra of $Cu_{2-x}Te$ samples with x=0-0.2 from four different experimental groups are collected and plotted in Fig. 5. The first one (red) is from the JCPDS database (PDF No. 10-1042) for the powdered samples, so only discrete peaks are shown. The other three (labeled as A, B, and C) are collected from the experimental literature published after 2000[31-34]. Although the peak intensity differs and some of the JCPDS peaks were not observed in the A, B and C spectra (maybe due to the different size of the powdered samples or different orientation of thin film and nanocrystal samples), the positions (2θ) of the high peaks in the A, B and C spectra agree with each other and can be reasonably matched to the high JCPDS peaks. There are slight shift in the peak positions, which should result from the small composition difference of the four samples. Considering that all the high peaks in A, B and C spectra are included the standard JCPDS peaks, we can compare our simulated XRD peaks to the JCPDS peaks.

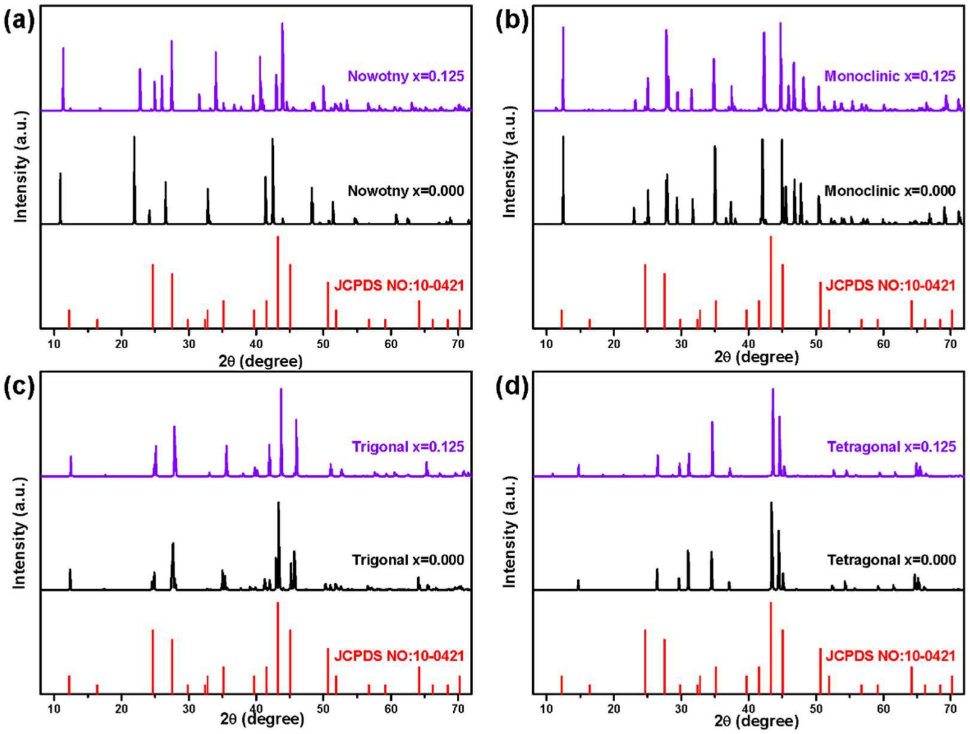

Figure 6. The simulated XRD spectra of $Cu_{2-x}Te$ (x=0 and 0.125) in (a) Nowotny, (b) monoclinic, (c) trigonal and (d) tetragonal structures. The nominal x-ray source is Cu Kα (λ =0.15406 nm). The experimental JCPDS peaks are also plotted for comparison.

In Fig. 6, the simulated XRD spectra of four $Cu_{2-x}Te$ structures after structural relaxation are plotted with both x=0 and x=0.125. The JCPDS experimental peaks are also plotted for comparison. Obviously the peaks of the Nowotny structures with both x=0 and 0.125 do not match the experimental peaks, so we predict that the possibility of Nowotny structures existing in the synthesized samples should be very small, especially considering that its energy is also high (at least 0.10-0.55 eV/f.u. higher than the most stable structure when $0<x<0.375$). For the monoclinic structures, their peaks around $2\theta=25, 27.5, 51^{o}$ match the experimental peaks well, however, the high peaks around $2\theta=43, 45^{o}$ do not match the experimental spectra. Similarly for the tetragonal structures, the peaks around $2\theta=43, 45^{o}$ match while those around $2\theta=26, 32^{o}$ do not match the JCPDS peaks. Among all the structures, the XRD spectra of the trigonal structures have the best agreement with the experimental spectra, i.e., all the high JCPDS peaks can be attributed reasonably to the simulated peaks. Since the most stable structure of $Cu_{2-x}Te$ changes from the monoclinic at x=0 to trigonal structure at x=0.125-0.625, the best agreement of the simulated XRD spectra indicates that the trigonal structures have a high possibility to exist in the synthesized $Cu_{2-x}Te$ samples with $0.125\leq x\leq 0.625$. Therefore the trigonal structures should be used in the future refinement of the experimental XRD spectra, while the high-energy Nowotny as well as monoclinic and tetragonal structures should be considered as the coexisting metastable phases of $Cu_{2-x}Te$ with $0<x\leq 0.625$ or as the stable phase of $Cu_{2-x}Te$ with $x>0.625$. It is noticed that tiny JCPDS peaks at $2\theta=30$ and 68^o cannot be attributed to the trigonal structure, which may result from the mixture of other phases such as the monoclinic one.

One question arises then. Why did the early experiments by Nowotny in 1946 attribute the samples to the hexagonal Nowotny structure[17]? To answer this question, we calculated the XRD spectrum of the Cu_2Te Nowotny structure with the lattice constants given in Nowotny's experimental paper[15,17], and plotted it in Fig. 5 (labelled as the experimental Nowotny structure). Good agreement can be found between the peaks of the experimental Nowotny structure and those from other experimental groups or the JCPDS database. Slight mismatch exists for the peak positions, which is reasonable because the composition (x) may differ in Nowotny's and other groups' samples. Since the experimental XRD spectrum of the powdered Cu_2Te sample (shown by the JCPDS peaks) can be well fitted using the Nowotny structure, we can understand why it was proposed experimentally as the structure of Cu_2Te by Nowotny[17]. The fitted lattice constants were a=4.237 Å, c=7.247 Å[15,17], but a first-principles structural relaxation can show clearly that the fitted lattice constants are not equilibrium lattice constants of the structure, which should be a=4.26 Å, c=8.11 Å according to our structural relaxation (the relaxation decreases the total energy by 0.1 eV/f.u.). A large difference (0.9 Å) in the c lattice constant can be found between the experimentally fitted and the theoretically relaxed lattice constants. Recent calculations by Zhang *et al.* using different exchange-correlation-functional approximations (local density approximation, generalized gradient approximation, DFT-D2 van der Walls correction) also predicted large c lattice constants (larger than 8.1 Å)[35], in agreement with our calculation. If we simulate the XRD spectrum of the Nowotny structure using the relaxed lattice constants, the spectrum (as shown in Fig. 6(a)) changes dramatically from that simulated using the experimentally fitted lattice constants, and thus does not match the experimental spectra or the JCPDS peaks any more. Simply speaking, the experimental XRD spectrum can be fitted using both the Nowotny structure and the trigonal structure, however, the Nowotny structure is not stable (the fitted lattice constants are not at equilibrium, and also the structure has a much higher energy than others), so it has a smaller possibility to exist in the synthesized samples than the trigonal structure. Based on this, we propose that the previous refinement of $Cu_{2-x}Te$ XRD spectra using the Nowotny structure should be reexamined using the trigonal structure.

IV. Conclusions

The structural transition of the binary $Cu_{2-x}Te$ compounds was studied based on the first-principles calculations. For stoichiometric Cu_2Te (x=0), our calculations show that the most stable structure is the monoclinic structure, which is consistent with the recent global structure search. However, our calculations also show that all the reported structures of stoichiometric Cu_2Te are metastable with respect to the phase separation $Cu_2Te \rightarrow Cu_{2-x}Te + xCu$. The formation of Cu vacancies in Cu_2Te is spontaneous from the thermodynamic point of view, and causes the structural transition of $Cu_{2-x}Te$ from the monoclinic (most stable when $x=0$), to trigonal ($0.125 \leq x \leq 0.625$), and then to hexagonal Nowotny structure ($0.75 \leq x < 1$). The simulated XRD peaks of the trigonal structures have the best agreement with the experimental spectra of the recently-synthesized $Cu_{2-x}Te$ samples with $x=0$-0.2, and also match the standard JCPDS peaks. Considering the lower energy and the good agreement of the XRD peaks, we predict that the synthesized $Cu_{2-x}Te$ samples (the Weissite mineral) should crystallize mainly in the trigonal structure, rather than the previously recognized Nowotny structure.

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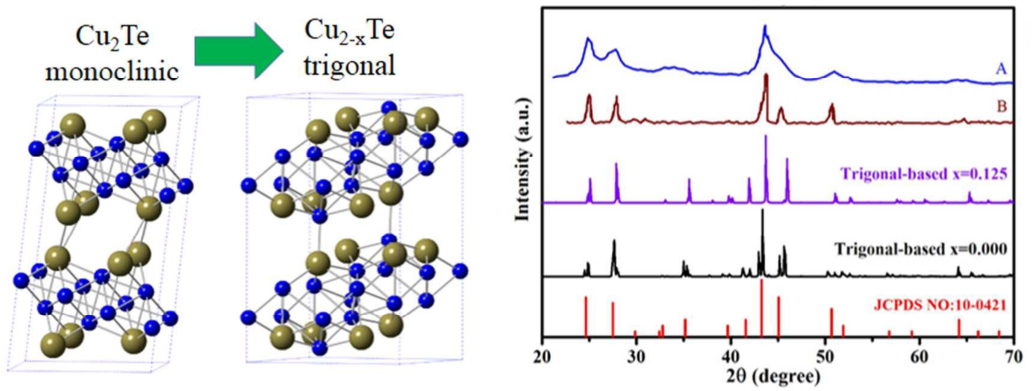
Graphical and textual abstract



All the reported structures of Cu_2Te are found to be metastable with respect to the phase separation $Cu_2Te \rightarrow Cu_{2-x}Te + xCu$, which causes a structural transition of $Cu_{2-x}Te$ from the monoclinic structure (stable when x=0) to trigonal structure ($0.125 \leq x \leq 0.625$). The experimental XRD peaks of $Cu_{2-x}Te$ samples should be attributed to the trigonal structure, rather than the previously recognized hexagonal Nowotny structure.