First-principles study for effect of lattice defects on the crystal structure of the Zn-Sc cubic crystalline approximant

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Abstract. Effects of impurity and vacancy introductions are investigated by the first-principles structural relaxation. Studied concentration of the lattice defects is 0.6 at%. As the impurity, a Cu atom is substituted for a Zn atom in Zn₆Sc. For this concentration, the plausible candidate site of Cu substitution is the glue site distributing in the interstitial region between icosahedral clusters. The most stable vacancy site is the core of the icosahedral cluster. Some of the introduced vacancies migrate several angstrom and reach the core. A special site being outside the core plays an important role for the vacancy migration. The vacancy introduced near this site migrates to the core. Significant Zn-Zn bonds are found in the charge density map. The stability of the defect-introduced structure is discussed in terms of a breaking of this bond.

1. Introduction
The binary quasicrystals Cd₅₋₇Yb/Ca are valuable samples for discussing the origin of the quasiperiodicity, because those are free from chemical disorder [1, 2]. The approximant crystals of those intermetallic compounds, Cd₆Yb/Ca and Zn₆Sc, have very close composition and structure to the quasicrystalline phase [1, 3]. Due to these similarities, the approximant phases are intensively investigated as a target of comparative studies for the quasicrystals. The approximant phases of this system have a notable feature that an order-disorder transition found around 100 K [4, 5, 6]. The order-disorder transition is considered to be attributed to orientational changes in the tetrahedral clusters located at the center of an icosahedral cluster. The icosahedral cluster, which is called Tsai-cluster, consists of four layered atomic shells: tetrahedron, dodecahedron, icosahedron and icosidodecahedron from inner to outer. The Tsai-cluster is a building block of not only the approximants but also quasicrystals [3]. But, interestingly, the transition is not found in the quasicrystalline phase. Although the reason why the quasicrystalline phase does not exhibit the transition has not been clarified yet, the transition would be incompatible with the quasiperiodicity. In this sense, the order-disorder transition may provide a clue to understand the quasiperiodic structure.

Recently, Yamada and Tamura investigated effects of lattice defects on the order-disorder transition in Zn-Sc system [7]. They found that Cu substitution of 0.1 at% for the Zn site lowers the transition temperature from 155 K to 100 K. Moreover the transition disappears by 0.5 at% substitution. They speculated that the ordering of the tetrahedral shell is suppressed
by the distortion of outer shells resulting from the Cu substitution. The atomic sites having a significant influence on the ordering of the tetrahedral shell are considered to be the tetrahedral shell itself or the dodecahedral second shell being just outside of the tetrahedral core. Lin and Corbett studied the crystal structure of \( \text{Zn}_{18-\gamma}\text{Cu}_\gamma\text{Sc}_3 \) \((\gamma=0.65, 1.48 \text{ and } 2.19)\), and concluded that Cu atoms occupy the dodecahedral shell [8], though the Cu concentration is rather higher than the experiment by Yamada and Tamura [7] \((\gamma=0.65 \text{ corresponds } 3.1 \text{ at%). In this paper, we study the substitution site by Cu in Zn-Sc systems using the first principles electronic structure calculation. If the distortion of the outer cluster suppresses the ordering of the tetrahedral core, atomic vacancies may do so as well. The atomic site capable to be a vacant site is also studied in this paper.

2. Calculation methods and systems

The density functional method within the local density approximation is used to calculate relaxed structures and those total energies. Calculations are done with a program package VASP [9, 10, 11, 12, 13, 14]. The ionic potentials are approximated by the ultrasoft pseudopotentials [15]. In this study, we treat the Zn-Sc, Zn-Cu-Sc systems. The number of electrons treated as the valence electrons are 12, 9 and 11 for Zn, Sc and Cu. The electronic wavefunctions are expanded by plane-wave basis set up to a kinetic energy of 209.6 and 233.8 eV for Zn-Sc and Zn-Cu-Sc systems, respectively. A cubic cell including 168 atoms is adopted as the unit cell. The unit cell contains two Tsai-clusters \((2 \times 66 \text{ atoms})\) and 36 glue Zn atoms. The Brillouin zone is sampled by \(3 \times 3 \times 3\) Monkhorst-Pack grids \((14 \text{ irreducible k-points})\). The atomic positions are fully relaxed according to the evaluated force obtained in each self-consistent calculation step.

One of the 168 sites in Zn\(_6\)Sc is substituted by Cu, i.e., the concentration of Cu is 0.6 at% comparable to the experiment by Yamada and Tamura \((0.5 \text{ at%})\) [7]. The substitution site can be classified according to the symmetry of the unit cell. The structure of the tetrahedral cluster determines the set of atomic sites for substitution, because it has the lowest symmetry. As the tetrahedral cluster, we adopted the one obtained as the most stable structure for Cd\(_6\)Ca by first-principles calculations [16]. It is also a candidate of the stable structure in Zn-Sc system [17]. The adopted tetrahedron is an appropriate subset of the 24g sites reported by a X-ray diffraction experiment for Zn\(_6\)Sc [8]. We assume that two tetrahedra in the unit cell, which are on the vertex and body-center of the cubic cell, face to the opposite direction. This orientational configuration is denoted as LCI structure in the references [16, 17]. Using the symmetry of the tetrahedral core, the substitution sites are classified into 28 inequivalent sites. Note that the icosahedral third shell, which is occupied by second elements (Sc) in pure system, is not assumed to be a substitution site, because the atomic size of Cu\((1.28 \text{ Å})\) is much smaller than Sc\((1.68 \text{ Å})\).

After the structural relaxation of Cu-introduced system \((\text{Zn-Cu-Sc})\), Cu atom is removed from the system in order to investigate the vacancy introduced system. In other words, the relaxed Cu-introduced systems are used as starting structures of structural relaxations for vacancy-introduced Zn-Sc systems. Thus the case where the vacancy is at the third shell is not studied. However it seems to be reasonable to consider that the majority element (Zn) is removed more easily than the minority one (Sc).

3. Results and discussions

3.1. Copper substitution

One of the Zn atoms in the cubic Zn\(_6\)Sc is replaced by Cu and the positions of the 168 atoms are fully relaxed according to the force obtained as a derivative of the calculated energy. The obtained total energies are listed in Table 1. The second column of the table denotes the total energy, and in the third column the relative energy from the most stable one is given. The most stable site for Cu substitution is the third glue-24g site, which is denoted as glue-24g-3 hereafter.
Note that the Wyckoff sites referred in this paper are the ones with Im\(\bar{3}\) symmetry and only for comparison with experiments. In the calculation, no constraint for symmetry is adopted and the system does not have Im\(\bar{3}\) symmetry even for the starting structure because the fractional sites in the first shell of Im\(\bar{3}\) model cannot be treated in the first-principles calculation. The glue-sites are the sites distributed in the interstitial region between Tsai-clusters. The stabilization mechanism of each site has not been understood well yet. Generally an impurity at the glue-24g sites gives lower energies. Some exceptions are found for glue-12e-3, glue-24g-5 and 2nd-24g-1.

From the obtained list of the total energies, we can say that the most favorable site for Cu substitution is the glue site in this concentration. Lin and Corbett performed the X-ray diffraction analysis for Zn-Cu-Sc system and concluded that the sites occupied by Cu are the 24g sites in the second shell [8]. But the concentration they studied is rather higher than in our case. The lowest concentration they studied includes about 2.6 atoms per Tsai-cluster (3.1 at%), but 0.5 (0.6 at%) in the present study. The favorable substitution site probably depends on the concentration. It would be interesting to compare these calculations with the ones done for higher concentrations.

### 3.2. Vacancy introduction

The Cu atom considered in the previous section is removed to describe the vacancy-introduced system. Accordingly, the concentration of the vacancy is also 0.6 at%. The atomic position of the rest of the 167 atoms in the cubic unit cell is re-relaxed. The evaluated total energy for each system is listed in Table 2 in the same manner as for the Cu substitution. One can find that the distribution of the relative energy is obviously different from that of Cu substitution. The glue sites which are concluded as the plausible candidates for the Cu substitution belong to the highest energy group. The lowest energy site is the 2nd-16f-1. But some sites give similar energies: 1st-2, 2nd-16f-2, 2nd-24g-2, -3, 5, 4th-48h-2, -3, -4 and -6. The relaxed structures of these ten cases are in fact the same. The energy difference between them is therefore considered as numerical errors. The most stable structure for the vacancy-introduced Zn-Sc system has only three Zn atoms in the cluster center forming a regular-triangle perpendicular to the threefold axes of the unit cell (the directions from the cluster center to the 2nd-16f sites). It is surprising that the vacancy introduced into the 4th shell migrates to the cluster center. If the vacancy is introduced into the second shell, one of the atoms of the first shell migrates to fill up the hole, and the rest three atoms of the first shell forms the regular-triangle. The hole in the 4th-shell is also filled up using this process. The 2nd-16f atom near the vacancy fills up the hole in the 4th-shell, then the first-shell’s atom goes outside to behave as the missing 2nd-16f. The obtained results can be classified into three types:

- **Type A:** the above-mentioned type, the introduced vacancy of which is filled up by neighboring atoms and the vacancy migrates to the first shell at the final. The stable structure of the first shell is the regular triangle facing to a 2nd-16f site.
- **Type B:** the vacancy migrates to the first shell, but the first shell does not reach the stable structure (the regular triangle).
- **Type C:** the vacancy remains at the initial position.

The classification is noted in the table. The vacancy introduced in the 2nd-24g-1 is not occupied by the first-shell’s atom completely. The structural relaxation may be stuck in the metastable state during migration of the first-shell’s atom to the 2nd-24g-1 site. Therefore a proper description is that an intermediate state between B and C.

Except for a few cases, the vacancy introduced in the first, second or fourth(48h) shells migrates to the first shell finally. The exceptions might be originated from the distortion of the Tsai-cluster. As shown in the Fig. 1, the second shell is distorted by the first shell. There is a trend that the vacancy introduced in the right-hand region in the figure seems to be easily
Table 1. The total and relative total energies for Cu substitution. The unit of energy is eV.

| Sites         | Total energy | Relative energy |
|---------------|--------------|-----------------|
| 1st           | -4.8220041E+03 | 0.167           |
| 2             | -4.8218426E+03 | 0.183           |
| 2nd-16f       | -4.8216444E+03 | 0.203           |
| 2             | -4.8218063E+03 | 0.187           |
| 2nd-24g       | -4.8230281E+03 | 0.065           |
| 1             | -4.8226232E+03 | 0.141           |
| 2             | -4.8224785E+03 | 0.120           |
| 3             | -4.8209150E+03 | 0.276           |
| 4             | -4.8222710E+03 | 0.141           |
| 4th-12d       | -4.8215608E+03 | 0.212           |
| 1             | -4.8219498E+03 | 0.173           |
| 2             | -4.8222511E+03 | 0.143           |
| 3             | -4.8224693E+03 | 0.121           |
| 4             | -4.8213196E+03 | 0.236           |
| 1             | -4.8216059E+03 | 0.207           |
| 2             | -4.8213638E+03 | 0.231           |
| 3             | -4.8216652E+03 | 0.201           |
| 4             | -4.8212565E+03 | 0.242           |
| 5             | -4.8216336E+03 | 0.204           |
| glue-12e      | -4.8222113E+03 | 0.147           |
| 1             | -4.8210742E+03 | 0.260           |
| 2             | -4.8232904E+03 | 0.039           |
| 3             | -4.8222139E+03 | 0.146           |
| glue-24g      | -4.8230305E+03 | 0.065           |
| 1             | -4.8231948E+03 | 0.048           |
| 2             | -4.8236760E+03 | 0.000           |
| 3             | -4.8233763E+03 | 0.030           |
| 4             | -4.8225418E+03 | 0.113           |

Table 2. The total and relative total energies for the vacancy introduction. The final structures classified into three types are also presented.

| Sites         | Total energy | Relative energy | Type |
|---------------|--------------|-----------------|------|
| 1st           | -4.7648571E+03 | 0.142           | B    |
| 2             | -4.7662634E+03 | 0.001           | A    |
| 2nd-16f       | -4.7662732E+03 | 0.000           | A    |
| 2             | -4.7662258E+03 | 0.005           | A    |
| 2nd-24g       | -4.7626236E+03 | 0.365           | B    |
| 1             | -4.7662720E+03 | 0.000           | A    |
| 2             | -4.7662555E+03 | 0.002           | A    |
| 3             | -4.7563540E+03 | 0.992           | C    |
| 4             | -4.7662571E+03 | 0.002           | A    |
| 4th-12d       | -4.7617290E+03 | 0.454           | C    |
| 1             | -4.7619388E+03 | 0.433           | C    |
| 2             | -4.7628535E+03 | 0.342           | C    |
| 3             | -4.7617324E+03 | 0.454           | C    |
| 4             | -4.7554261E+03 | 1.085           | C    |
| 1             | -4.7662653E+03 | 0.001           | A    |
| 2             | -4.7662391E+03 | 0.003           | A    |
| 3             | -4.7662682E+03 | 0.001           | A    |
| 4             | -4.7560934E+03 | 1.018           | C    |
| 5             | -4.7662720E+03 | 0.000           | A    |
| 4th-48h       | -4.7613425E+03 | 0.493           | C    |
| 1             | -4.7607770E+03 | 0.550           | C    |
| 2             | -4.7629842E+03 | 0.329           | C    |
| 3             | -4.7615365E+03 | 0.474           | C    |
| glue-12e      | -4.7578792E+03 | 0.839           | C    |
| 1             | -4.7570832E+03 | 0.919           | C    |
| 2             | -4.7572245E+03 | 0.905           | C    |
| 3             | -4.7569326E+03 | 0.934           | C    |
| 4             | -4.7572637E+03 | 0.901           | C    |
filled up compared with that introduced in the left-hand region. We should pay attention to the energies of the 2nd-24g-4, 4th-48h-1 and 4th-48h-5. Those are the ones classified as type C, the vacancy of which does not migrate to the first shell. When the vacancy remains at these sites, the system is considerably less stable than others (4th-12d and glue-12e sites). Fig. 2 is a charge density map of the ideal Zn\(_6\)Sc without defects. The displayed charge density is the difference charge density: \(\rho = \rho\text{(SCF)} - \rho\text{(atom)}\), where \(\rho\text{(SCF)}\) is the charge density obtained by the SCF calculation and \(\rho\text{(atom)}\) is the one given as a superposition of the charge of isolated atoms. Thus in a rough description the positive value of the difference charge density means a bonding trend around the region. The positive value is shown only in the figure. The red, blue, green and black balls in the figure denote the atoms of the first, second, third and fourth shells.

One can find a significant increase of the difference charge density on lines connecting the blue balls (second-shell’s atom). The charge clouds forming triangles around the 2nd-16f sites are originated from the bond between the the second- and fourth-shell’s atoms. By the replacement of these atoms with a vacancy, the significant bond is broken. Present results imply that the energy loss of the bond-breaking is rather large, because the total energy of the 2nd-24g-4, 4th-48h-1 and 4th-48h-5 is twice as large as the other cases of the 4th-12d and glue-12e.

**Figure 1.** The Tsai-cluster is distorted by the tetrahedral core. The red and blue balls represent the atoms of first and second shells.

**Figure 2.** The difference charge density map in complete Zn\(_6\)Sc. The significant increase in the charge density is found on the line connecting the second shell.

The vacancies introduced at the glue or 4th-12d sites do not migrate to other sites. This is because the 2nd-16f sites are not around these sites. In the case that the 4th-48h sites are filled up successfully, these sites have a 2nd-16f site as the nearest neighbor (NN) or next nearest neighbor (NNN), and the atoms at the 2nd-16f sites fill the vacancies without exception. The NN and NNN of 4th-12d sites are the 2nd-24g or other 4th-12d sites. As for the glue sites, those are other glue sites. Although the reason of that has not been understood, we can say that the 2nd-16f site would be easily migrate outer shells in comparison with the 2nd-24g sites.

4. Summary
We performed first-principles structural relaxations to investigate the crystal structure of lattice-defects-introduced Zn-Sc cubic approximants. The lattice defects studied are the atom (Cu) substitution and vacancy introduction. The concentration of the impurities is 0.6 at%, which
means a single impurity in the cubic unit cell. The most plausible site for Cu substitution is concluded as the glue sites for this concentration. As for the vacancy introduction, some vacancies introduced in the second and fourth shells migrate to the first shell. It may imply the existence of a strong bond between the second and fourth shells. The total energies of the case that the vacancies remain at the introduced sites are explained by breaking of the significant bonds. Two trends for the mobility of the vacancies are found. One is concerned with the distortion of the Tsai-cluster. The vacancy introduced in a distorted part is easily filled up by a neighboring atom. Another one may indicate a special character of the 2nd-16f site. The vacancies introduced in the fourth shell are filled up by an atom at 2nd-16f sites without exception. The vacant sites far from the 2nd-16f site are not filled up. The 2nd-16f site seems to migrate easily from the initial position in comparison with the 2nd-24g site. In the quasicrystalline phase, the dodecahedral shell is not distorted [3]. The 16f site is no longer a particular site in that phase, because the 16f and 24g sites discussed here is equivalent. Therefore the special character of the 16f site, or the threefold linkage between Tsai-clusters, in the approximant phase may be deeply related with the origin of the order-disorder transition, which has not been found in the quasicrystalline phase.

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