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First Principles Calculation of Defect Structure in Non-stoichiometric CoAl and CoTi

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First-principles electronic structure calculations have been performed for defect structure in non-stoichiometric CoAl and CoTi. In order to determine the type of constitutional defects, the compositional dependence curves both of formation energies and of lattice parameters are obtained by the calculations employing supercells in various sizes. The defect formation energies are calculated with taking into account the compositional dependence of the chemical potential. The calculated results suggest that the Co vacancy is the dominant thermal-excitation defect even in the Co-rich side near the stoiciometry in CoTi.

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1. Introduction

Intermetallic compounds with the B2 structure have attracted considerable attention as promising candidates for high-temperature materials. One of the important features of intermetallic compounds with the B2 structure is having a wider range of compositions than other phases. In order to compensate the deviation from the stoichiometry, constitutional defects are introduced. Several properties such as mechanical and magnetic properties, therefore, show compositional dependence originating from the constitutional defects. In addition, thermally excited defects play an important role in the diffusion of atoms and therefore the understanding of the defects are required for the alloy design and optimization of heat treatment.

Electronic structure calculations using supercell models have been performed for non-stoichiometric B2 intermetallic compounds to understand the defect structure. The size of the supercell is one of the important factors for electronic structure calculations including defects. The defect formation energies in FeAl were calculated using the 8, 16 and 32 atoms supercells.[1] The calculations with the 16 and 54 atoms supercells were performed for convergence tests of the effective formation energies and the structural relaxation of the constitutional defects in NiAl.[2] In our previous work, we obtained formation energy curves of CoAl and CoTi including constitutional defects by performing electronic structure calculations with various sizes of supercell models.[3] Whereas the formation energy curve of CoAl shows almost linear change for its composition, that of CoTi has a curvature at around $Co_{51}Ti_{49}$ including Co antisite atoms. This result indicates that the chemical potential of Co and Ti varies at around this composition. In this case defect formation energies, which are calculated using chemical potentials, could show a compositional dependence.

In this paper, we have performed first-principles electronic structure calculations in order to determine the defect structure in non-stoichiometric CoAl and CoTi. The various sizes of supercells are employed in order to obtain the composition dependence curves both of formation energies and free energies. The stability of the constitutional defects is evaluated by the compositional dependence curves of formation energies. The defect formation energies are obtained with taking into account the compositional dependence of chemical potentials.

2. Computational Method

In order to obtain the electronic structures for the constitutional defects, we employed first-principles plane-wave pseudopotential code VASP (Vienna *ab initio*) simulation package[4,5] with generalized gradient approximation proposed by Perdew and Wang.[6] First, we calculated the equilibrium lattice constant using the kinetic energy cutoff of 350 eV and a $16 \times 16 \times 16$ k-mesh in the Monkhorst-Pack scheme with the unit cell including 2 atoms. The Ti-3p electrons were treated as valence electrons. We obtained the equilibrium lattice constant of 0.2855 nm for CoAl and 0.2982 nm for CoTi, which reproduces the experimental values within 1%. We estimate the stability of the constitutional defects by the formation energies of CoAl and CoTi including the constitutional defects. The formation energies were calculated by subtracting the total energy of constituent elemental solids from the total energy of the compounds. In order to compare the formation energies among various chemical compositions, the formation energies were calculated using the supercells with various sizes ($2 \times 2 \times 2$, $3 \times 3 \times 3$ and $4 \times 4 \times 4$), in which the central atom was replaced by a defect and we obtained the composition dependence curves of the formation energies. The total numbers of the lattice site, N, in the $2 \times 2 \times 2$, $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells are 16, 54, and 128, respectively. For the defect calculations, relaxations of the atomic positions were allowed. The equilibrium lattice parameter of the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells including a defect was obtained by performing calculations at several volumes and fitting the universal binding energy curve of Rose *et al.*[7] For the $4 \times 4 \times 4$ supercells, an interpolated lattice parameter was employed. The calculations of all sizes of the supercell models were done using a $6 \times 6 \times 6$ k-mesh, because a $6 \times 6 \times 6$ k-mesh is required for the sufficient convergence of the lattice relaxation.[3]

The defect formation energies can be calculated using the defect energy parameters and the chemical potentials.[1] The defect energy parameters are defined as the energy difference between of the supercell including the defect and of the ideal supercell of N atoms. In the case of AB compound with A atoms on the α and B atoms on the β sublattices,

$$\varepsilon_{\mathrm{V}}^{\alpha} = E(N-1, V^{\alpha}) - E(N, 0), \tag{1}$$

$$\varepsilon_{\mathrm{A}}^{\beta} = E(N-1, A^{\beta}) - E(N, 0). \tag{2}$$

$\varepsilon_{\mathrm{V}}^{\alpha}$ and $\varepsilon_{\mathrm{A}}^{\beta}$ is the defect energy parameter for the formation of a vacancy on the α sublattice and for the formation of an A antisite atom on the β sublattice, respectively. In general, the concentration of the thermally excited defects is much smaller than that of the defect concentration of supercells employed in first-principles electronic structure calculations. Therefore we checked the convergence of the defect energy parameters for supercell size. Figures 1 and 2 shows the dependence of the defect energy parameters of the vacancies in CoAl and CoTi on the supercell size, respectively. The defect energy parameters except for the Co vacancy in CoAl exponentially decrease with the supercell size. The defect energy parameters of the antisite atoms show the same trend. These results suggest that the energy convergence of the $3 \times 3 \times 3$ supercell is expected to be within 0.2 eV. And that of the $4 \times 4 \times 4$ is within 0.02 eV. In the case of the Co vacancy in CoAl, the electron density of the second-nearest neighbor Co atoms increases by the formation of the Co vacancy.[3] The interaction between the second-nearest neighbor atoms is still significant in the $3 \times 3 \times 3$ supercell and therefore the defect energy parameter of the Co vacancy obtained by the $3 \times 3 \times 3$ supercell is higher than that of the other defects. We employed the energies of the $4 \times 4 \times 4$ supercells to calculate the defect energy parameters. The chemical potentials, μ, are used for the compensation of the energy of the atoms related to the defect formation. When calculating the defect formation energies of a vacancy on the α sublattice and that of an A antisite atom on the β sublattice,

$$E_{\mathrm{V}}^{\alpha} = \varepsilon_{\mathrm{V}}^{\alpha} + \mu_{\mathrm{A}}, \tag{3}$$

$$E_{\mathrm{A}}^{\alpha} = \varepsilon_{\mathrm{A}}^{\alpha} - \mu_{\mathrm{A}} + \mu_{\mathrm{B}}, \tag{4}$$

In most of previous works, the chemical potentials are obtained using the calculated energies of fixed-size supercells. This is based on the assumption that the chemical potentials change linearly with the composition. In this work, in order to taking into account the compositional dependence of the chemical potentials, they are obtained from interceptions at 0 and 100 at%Al/Ti of the tangent lines for the interpolation curve for the energies of the $2 \times 2 \times 2$, $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells.

Regarding the defect formation parameter of constitutional defects, the eqs. (1) and (2) are not applicable because the concentration of constitutional defects is much larger than thermally excited defects. While the defect formation parameter can be calculated using a slope of the energy curve, the defect formation energy of constitutional defects result in zero because the chemical potential cancel out the defect energy parameter by definition.

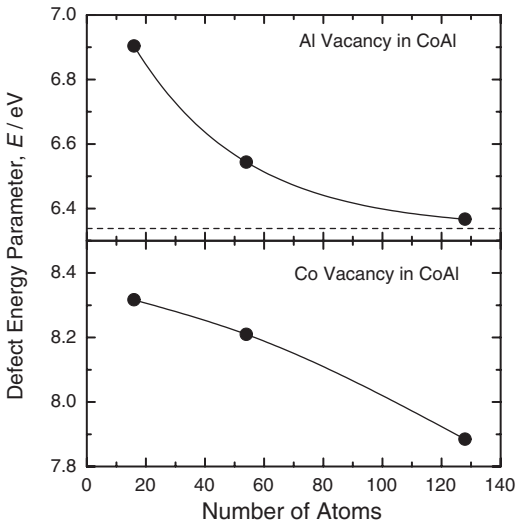

Fig. 1 Dependence of the defect energy parameters of vacancies in CoAl on the supercell size.

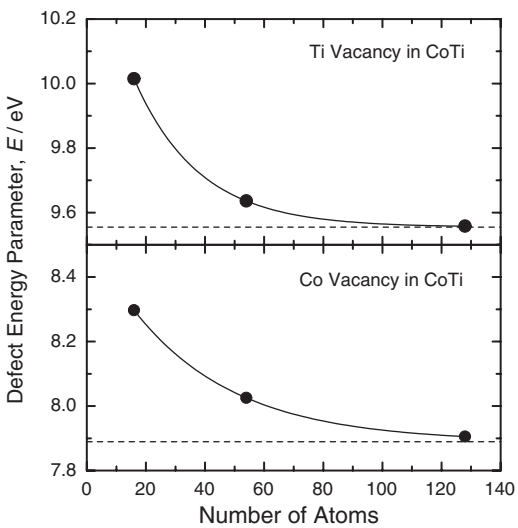

Fig. 2 Dependence of the defect energy parameters of vacancies in CoTi on the supercell size.

3. Results and Discussion

3.1 Stability of constitutional defects

Figures 3 and 4 show the formation energies as a function of the Al composition in CoAl and the Ti composition in CoTi, respectively. The open marks represent the formation energy obtained without the structural relaxation. In the Co-rich side both of CoAl and of CoTi, the Co antisite atoms are more stable than the Al/Ti vacancy, which indicates that the Co antisite atoms are introduced as constitutional defects. In particular, the formation energy for the Co antisite in CoTi is significantly lowered by the structural relaxation near the stoichiometry in the Co-rich side. On the other hand, in the Al-rich CoAl, the Co vacancy is slightly more stable than the Al antisite defect, while the Ti antisite defect shows lower formation energies than the Co vacancy in CoTi.

Paying attention to the shape of the formation energy curves, most of the formation energy changes almost linearly with the composition. However, a curvature appears in the

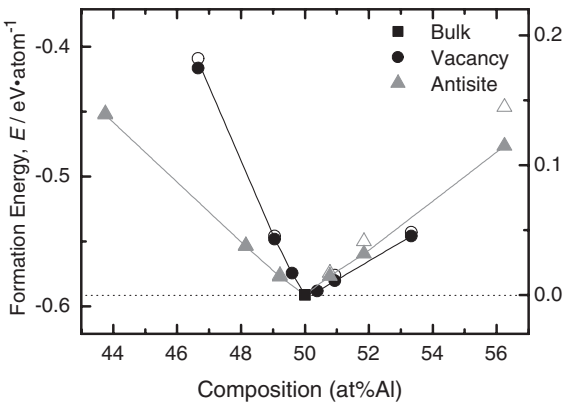

Fig. 3 The formation energy of CoAl including a constitutional defect as a function of Al composition. Open marks represent the results without the structural relaxation.

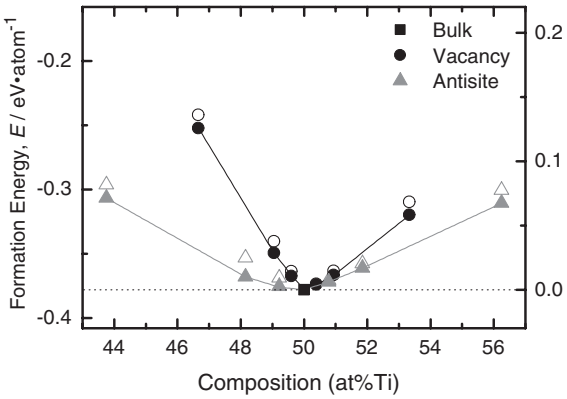

Fig. 4 The formation energy of CoTi including a constitutional defect as a function of Ti composition. Open marks represent the results without the structural relaxation.

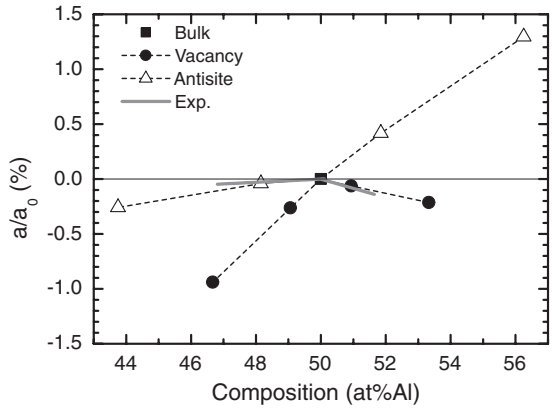

Fig. 5 The lattice parameter of CoAl including a constitutional defect as a function of Al composition. Experimental data were measured by Kogachi *et al.*[8)]

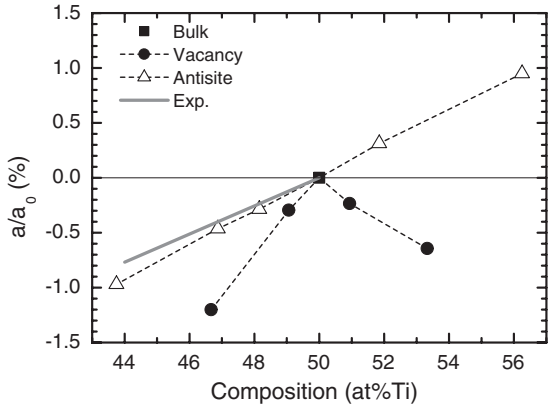

Fig. 6 The lattice parameter of CoTi including a constitutional defect as a function of Ti composition. Experimental data were measured by Aoki *et al.*[9)]

Co-rich side of CoTi near the stoichiometric composition because of the structural relaxation. The detail of the structural relaxation will be discussed latter.

The change in the lattice parameter in CoAl and CoTi is shown in Figs. 5 and 6, respectively. The lattice parameters are normalized by the equilibrium lattice parameter of the stoichiometric composition. The general trend for the change in the lattice parameter is similar between CoAl and CoTi. The vacancies of Ti and Al atoms, which have larger atomic radius than Co atom, have a larger influence of decreasing the lattice constant. The Co antisite also reduces the lattice constant, while the Ti and Al antisite expand it. These results are in accordance with the expectation from the atomic radius difference. The decrease of the lattice parameter by the deviation from the stoichiometry is more significant in CoTi than in CoAl. Comparing to the experimental results, we can conclude that the Co antisite atoms are introduced in compensation for the deviation from the stoichiometry in the Co-rich side of both CoAl and CoTi, and so do the Co vacancies in the Al-rich side of CoAl. These results agree well with the hierarchy of formation energies shown in Figs. 3 and 4. However, it seems difficult to identify the constitutional defects in the Ti-rich side of CoTi because of the narrow compositional range in the Ti-rich side. In this work, the Ti antisite atoms are considered as constitutional defects and the energy curve of the Ti antisite atoms is employed to obtain the chemical potential in the Ti-rich side of CoTi.

3.2 Structural relaxation around defects

Figures 7 and 8 show the amount of structural relaxation of nearest-neighbor atoms around the defects and the change in energy by the structural relaxation as a function of the defect concentration. The general trend of the relaxation is that the amount of relaxation decreases with the defect concentration owing to the increase of the interaction between the defects. On the other hand, the change in energy by the structural relaxation is proportional not only to the defect concentration but also the amount of the relaxation. There is a local maximum in the change in energy for the Co antisite and the Ti vacancy of CoTi in which more than 5% structural relaxation occurs at the low defect concentration. This local maximum appears as a curvature in the formation energy curve shown in Fig. 4. The chemical potentials vary markedly near the curvature, which leads to the compositional dependence of defect formation energies as discussed later.

The large outward relaxation around the Co antisite and Ti

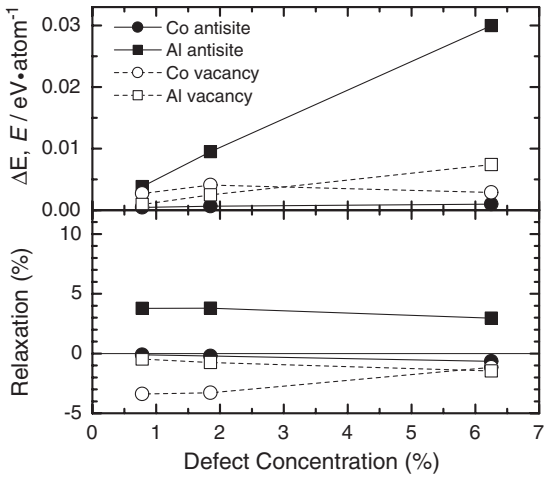

Fig. 7 The amount of structural relaxation of nearest-neighbor atoms around the defects (lower panel) and the change in energy by the structural relaxation (upper panel) as a function of the defect concentration in CoAl.

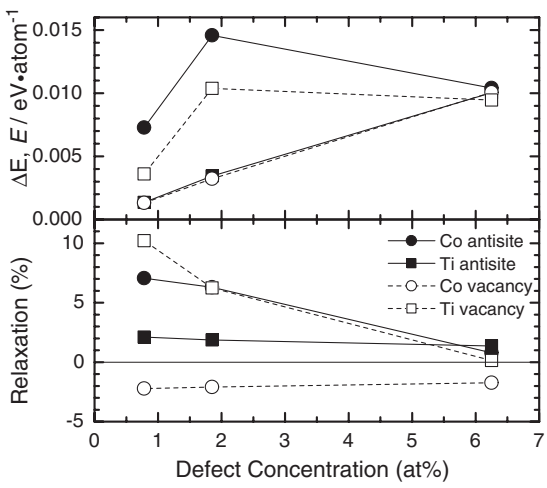

Fig. 8 The amount of structural relaxation of nearest-neighbor atoms around the defects (lower panel) and the change in energy by the structural relaxation (upper panel) as a function of the defect concentration in CoTi.

vacancy cannot be explained by the atomic size difference. The inward relaxation is expected to occur because the atomic radius of Ti is about 15% larger than that of Co. These unexpected relaxations arise from the charge redistribution around the defects.[3] The charge transfer from Ti to Co occurs in CoTi. The Ti vacancy, which is surrounded by the negatively charged Co atoms, has a repulsive potential for electrons. As a result, the electrons are repelled away from the Ti vacancy and are redistributed to the Co–Ti bonding outside the Ti vacancy. The Co atoms around the Ti vacancy move away because of the increase of the bonding electrons of the Co–Ti bonds. The similar charge redistribution occurs around the Co antisite in CoTi. Whereas the outward relaxation of neighboring atoms around a vacancy observed in ionic compounds such as MgO is mainly caused by the Coulomb repulsion between neighboring atoms, the outward relaxation in CoTi originates from the mixture of the ionic and covalent bondings. The outward relaxation against the atomic size difference is not observed in CoAl, because the

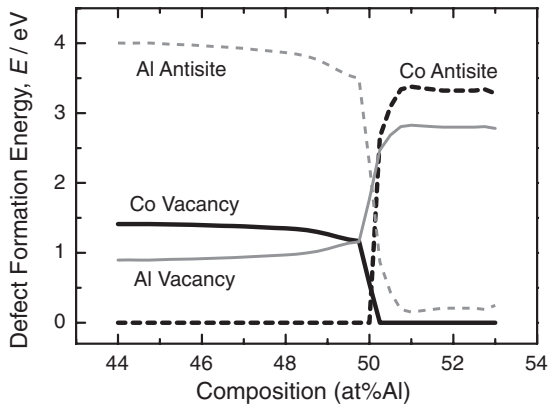

Fig. 9 The defect formation energies for CoAl as a function of Al composition.

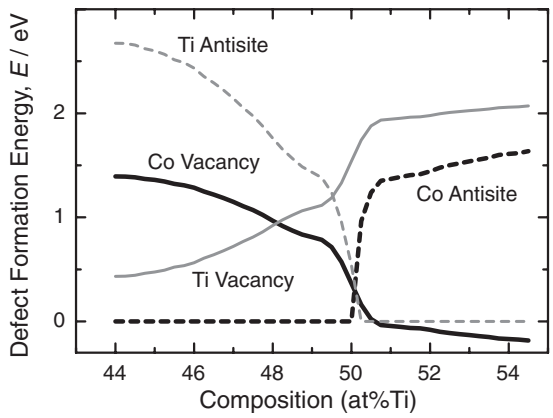

Fig. 10 The defect formation energies for CoTi as a function of Ti composition.

amount of the charge transfer from Al to Co in CoAl is smaller than that from Ti to Co in CoTi.[3,11]

3.3 Defect formation energies

The calculated defect formation energies for CoAl and CoTi are shown in Fig. 9 and Fig. 10, respectively. The defect formation energies of defects treated as constitutional defects are zero as mentioned in Section 2. Those for CoAl are almost constant except for around the stoichiometric composition. This is because the energy curve changes almost linearly for the composition as seen in Fig. 3. Comparing to the previous work using the defect energy parameters calculated by the $3 \times 3 \times 3$ supercells,[9] the defect formation energies for CoAl show the same trend. However, the values of the defect formation energies in this work are 0.1–0.5 eV smaller than those of the previous work, since we employed the defect energy parameters obtained by the $4 \times 4 \times 4$ supercells. In contrast to CoAl, the defect formation energies for CoTi shows the significant compositional dependence in the Co-rich side. Whereas it is natural to expect that the Ti vacancy is more favorable than the Co vacancy in the Co-rich side, the formation energy of the Co vacancy is lower than that of the Ti vacancy near the stoichiometric composition in the Co-rich side. This is because the chemical potential of the Co atom is lowered

because of the curvature of the energy curve caused by the large structural relaxation around the Co antisite atoms. This is in agreement with the experimental work using positron lifetime measurement suggesting that the Ti vacancy is not formed even in the Co-rich side of CoTi.[11] However, a discrepancy is also observed in the less than Ti 48 at%. While the calculated formation energy of the Ti vacancy is lower than that of the Co vacancy in this composition range, the Ti vacancy is not still observed by the positron lifetime measurement. The Ti vacancy turns into a complex of the Co vacancy and the Co antisite atom by one nearest-neighbor jump of the Co atom. In order to examine the stability of this type of defect complex in CoAl and CoTi, we compare the energy obtained by the $3 \times 3 \times 3$ supercell with or without structural relaxation.

$$\begin{aligned} &\mathrm{CoAl} : \mathrm{Al_V} \rightarrow \mathrm{Co_V} + \mathrm{Co_{Al}}; \\ &\quad \Delta E_{\mathrm{fixed}} = 0.35\,\mathrm{eV}, \\ &\quad \Delta E_{\mathrm{relaxed}} = 0.10\,\mathrm{eV} \end{aligned} \tag{5}$$

$$\begin{aligned} &\mathrm{CoTi} : \mathrm{Ti_V} \rightarrow \mathrm{Co_V} + \mathrm{Co_{Ti}}; \\ &\quad \Delta E_{\mathrm{fixed}} = 0.28\,\mathrm{eV}, \\ &\quad \Delta E_{\mathrm{relaxed}} = -0.38\,\mathrm{eV} \end{aligned} \tag{6}$$

This result clearly indicates that the complex of the Co vacancy and the Co antisite is stabilized by the structural relaxation. As seen in Fig. 8, the large outward relaxation occurs around the Co antisite and Ti vacancy in CoTi. In the complex of the Co vacancy and the Co antisite, the Co antisite, which exhibits the outward relaxations around it, could reduce the inward relaxation around the Co vacancy leading to the stability of the defect complex. We plan to confirm the formation of the Co vacancy in the Co-rich CoTi using coincidence Doppler broadening measurement[12] that can be used to identify the neighboring atoms around vacancies.

4. Summary

We have performed the first-principles electronic structure calculations of non-stoichiometric CoAl and CoTi in order to determine the defect structure in non-stoichiometric CoAl and CoTi. The composition–dependence curves of both the formation energy and the lattice parameter well explain the formation of constitutional defects to compensate for the deviation from the stoichiometric composition. Although the change in lattice parameter induced by the constitutional defect obeys the difference in atomic radius, the local relaxation around it shows unexpected behavior. In particular, the nearest-neighbor Co atoms around the Co antisite and the Ti vacancy in CoTi show large outward displacements. Because of the large outward displacements, the energy curve of CoTi has a curvature in the Co-rich side near the stoichiometric composition, which leads to the change in the chemical potentials. The defect formation energy for CoTi, therefore, shows compositional dependence in the Co-rich side and indicates that the formation of Co vacancy is expected even in the Co-rich side near the stoichiometry. The defect complex of the Co antisite and Co vacancy is also expected in the composition in which the formation energy of the Ti vacancy is lowered than that of the Co vacancy.

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