Theoretical Calculation of Positron Lifetimes in CoAl and CoTi

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1. Introduction

Intermetallic compounds are of considerable interest due to their physical and mechanical properties. In intermetallic compounds having a wide range of concentrations around the stoichiometry, structural defects are introduced in order to compensate deviations from the stoichiometry. Several properties show compositional dependence originating from the structural defects. Main structural defects are vacancies on the sublattice and anti-structure atoms occupying the other sublattice.

Positron annihilation spectroscopy is a sensitive tool for vacancy-type defects in solids. In a perfect crystal, the positron wave function is delocalized in the interstitial region because of the repulsion from the ion cores. If vacancy-type defects exist in solids, the positron wave function is localized at the defect where the electron density is lower than the other regions. The localization of the positron at the defect results in a longer lifetime of the positron compared to the bulk lifetime because the positron lifetime is inversely proportional to the electron density where the positron annihilated. Positron annihilation spectroscopy is very useful to study the behavior of the structural defects in intermetallic compounds. If the vacancy is mainly responsible for the deviation from the stoichiometry, longer positron lifetimes should be measured compared to the bulk lifetime. However, interpretation of the experimental positron lifetime for intermetallic compounds is more complicated than for pure metals, because several types of vacancies may exist in intermetallic compounds. The different types of vacancies may yield the different positron lifetimes. In order to characterize measured positron lifetimes in intermetallic compounds, a theoretical analysis is indispensable. However, little theoretical work has been done for intermetallic compounds.

In this work, we have performed calculations of positron lifetimes in intermetallic compounds CoAl and CoTi with the B2 structure based on first-principles electronic structure calculations. The calculated results are compared with the experimental positron lifetimes in order to identify the defect type in intermetallic compounds and estimate the reliability of the calculated positron lifetimes.

2. Computational Method

In order to obtain the electron density and potential, the DV-Xα cluster method using a program code SCAT1,2) is employed. In this first-principles calculation, the molecular-orbital wave function is expressed by a linear combination of atomic orbitals (LCAO). The molecular orbital wave function is expressed by a linear combination of atomic orbitals (LCAO) and is written as

\[ \phi_i = \sum l c_{il} \chi_l, \]

where \( c_{il}'s \) are coefficients. As the basis function \( \chi_l \), we use the numerical atomic orbitals obtained by solving the radial part of the Schrödinger equation for each atom in a given environment. 1s-4p and 1s-3d atomic orbitals are used for 3d transition metals and Al atoms, respectively. In order to obtain the orbital populations and the overlap populations, the Mulliken population analysis3) is performed. The orbital population, \( Q_i(l) \), and the overlap population, \( Q_{ij}(l) \), of the \( l \)th molecular orbital between \( \chi_i \) and \( \chi_j \) are defined by

\[ Q_i(l) = \sum_{j} f_i C_{il} C_{jl} \sum_k \omega(r_k) \chi_i(r_k) \chi_j(r_k), \]

\[ Q_{ij}(l) = \sum_{j} f_i C_{il} C_{jl} \sum_k \omega(r_k) \chi_i(r_k) \chi_j(r_k), \]

where \( f_i \) is the occupation number of the \( l \)th molecular orbital, and \( r_k \) is one of the sample points and \( \omega(r_k) \) is the integration weight for the sample point. The orbital population is useful to determine the effective atomic charge. The bond overlap population between A and B atoms is given by

\[ Q_{AB} = \sum_{i \in A} \sum_{j \in B} \sum_l Q_{ij}(l). \]

The overlap population can be used as a measure of strength of the covalent bonding. Net charge of each atom...
\[ \Delta Q_A \text{ is obtained by} \]
\[ \Delta Q_A = Z_A - \sum_{i \in A} Q_i, \quad (5) \]

where \( Z_A \) is the atomic number of atom \( A \).

The model clusters composed of 113 atoms are used for the bulk state. The central atom is extracted for the calculation of the vacancy state. The three-dimensional potential \( V_+ (r) \) sensed by positron is constructed as a sum of the electron static potential \( V_c (r) \) due to the nuclei and the electrons, and a correlation potential \( V_{\text{corr}} (n_- (r)) \) describing the electron-positron correlation:

\[ V_+ (r) = V_c (r) + V_{\text{corr}} (n_- (r)), \quad (6) \]

where \( n_- (r) \) is the electron density. For the density dependence of \( V_{\text{corr}} (n_- (r)) \) we have used the interpolation formula by Puska et al.\(^4\) based on Lantto's data.\(^7\) The Schrödinger equation for the positron is solved by the finite-deference method\(^6\) employing the periodic boundary conditions for delocalized positron wave function in the bulk state. In the case of the localized positron at the vacancy, the boundary conditions are the vanishing of the positron wave function on the surface of a large polyhedron.

The positron lifetime \( \tau \) is calculated as the reciprocal value of the positron annihilation rate \( \lambda \) by

\[ \lambda = \frac{\pi r_0^2 c}{\int n_+ (r)n_- (r) \gamma (r) dr}, \quad (7) \]

where \( r_0 \) is the classical electron radius, \( c \) is the speed of light, \( n_+ (r) \) is the positron density and \( \gamma (r) \) is the enhancement factor describing the short-range pileup of the electron at the positron. For the enhancement factor, we have used the interpolation formula by Puska et al.\(^5\) based on Lantto’s data.\(^7\)

Partial annihilation rates are obtained using the results of the Mulliken population analysis.

3. Results and Discussion

3.1 Electronic structures

The partial and total density of states (DOS) and overlap population diagrams for bulk CoAl and CoTi are shown in Fig. 1 and Fig. 2, respectively. The DOS curves are made by broadening the discrete energy levels by Gaussian function of 0.5 eV full width at half-maximum (FWHM). The overlap population diagrams are obtained by convoluting the overlap population at each molecular orbital with Gaussian function. These curves are shifted so as to set the Fermi level at zero. The value written in each panel is the bond overlap population (BOP) obtained by summing up the overlap population at each molecular orbital over the occupied states. In CoAl, the low-lying Al 3s-3p band mainly interacts with Co 3d-4p orbitals. The bonding states between Co and Al are located from the bottom of the valence band up to the conduction band, whereas the anti-bonding state is almost unoccupied. The main peak of the Co 3d band in CoTi is located below the Fermi level and the position is slightly lower than that in CoAl. The Ti 3d band is positioned above the Co 3d band, which indicates that the charge transfer occurs from Ti to Co. Several authors have reported calculated DOS for CoAl\(^8\)-\(^{14}\) and CoTi\(^15\)-\(^17\) The general futures of our DOS are similar to those in the previous works. The bonding states between Co and Ti mainly arise from the interaction between Co 3d and Ti 3d bands. Compared with the Co–Al bonding in CoAl, the peak value of the overlap population around \(-2 \text{ eV}\) is larger; but the width of the bonding states is not so broad. The antibonding states of the Co–Ti bond are partially occupied. As a result, the BOP of the Co–Ti bond in CoTi is smaller than that of the Co–Al bond in CoAl.

Figure 3 shows net charge in CoAl and CoTi for the bulk and vacancy states. In the case of the vacancy, the net charges of the nearest neighbor atoms from the vacancy are plotted. It is clearly seen that the charge transfer in CoTi is larger than in CoAl. The vacancy in CoTi reduces the amount of the charge transfer, whereas the net charges in CoAl is hardly affected by the creation of the vacancy. These results suggest that the ionic contribution to the chemical bonding is more significant in CoTi.

3.2 Positron lifetimes

The calculated positron lifetimes and annihilation rates for CoAl and CoTi are listed in Table 1 and Table 2, respectively.
The positron lifetimes of the bulk state are almost same values for CoAl and CoTi. However, the annihilation rates show different trends. The Al and Co atoms have almost the same contribution to the positron annihilation rate in bulk CoAl. In bulk CoTi, the Ti atoms have larger contribution than the Co atoms. These results suggest that the distribution of positron wave function is larger around the Ti atoms than the Co atoms in bulk CoTi. The difference in distribution of the positron wave function causes the different positron lifetimes of the vacancy state described as follows. In contrast to the similar lifetime in bulk CoAl and CoTi, the trend for the positron lifetime of the vacancy state is not the same. In the case of the vacancy state in CoAl, the difference of positron lifetimes between the Co and Al vacancies is about 10 ps. In CoTi, the lifetime difference is larger than in CoAl. It is also interesting to note that the Co vacancy lifetime in AlCo is 50 ps longer than that in CoTi. This discrepancy arises from the difference in localization of the positron wave function at the vacancy. Because the positron annihilation rate is proportional to the overlap between the electron and the positron, a longer lifetime is expected for the positron better localized at the vacancy where the electron density is lower than other region. Figures 4 and 5 show the positron densities at the vacancy in CoAl and CoTi, respectively. At the Co vacancy in CoTi, the positron density is the lowest, which leads to the shortest positron lifetime of 135 ps. On the other hand, the difference in the positron density between the Co and Al vacancy in CoAl is not so large as in CoTi. The charge transfer induces the difference of the Coulomb potential at the vacancy and affects the localization of the positron trapped at the vacancy. Figure 6 shows the potential sensed by the positron localized at the vacancy. Owing to the charge transfer from Ti to Co in CoTi, the potential around the Co vacancy surrounded by positively charged Ti atoms is less attractive than that in CoAl. As a result, the positron wave function at the Co vacancy in CoTi is not well localized and yields the shorter lifetime.

### 3.3 Comparison with the experimental results

The experimental results for CoAl and CoTi are presented in Figs. 7 and 8, respectively. CoAl crystallizes in the B2 structure over a wide range of concentrations around stoichiometry: from 46–58 at%Co. The compositional range for CoTi is narrower: from 49–54 at%Co. The experimental...
mean-positron lifetime in CoAl increased with the increase of the Al composition. If the only one type structural vacancy exists, there is no dependence of the positron lifetime on the composition. The increase of the positron lifetime suggests that both the Al and Co vacancies exist and the amount of the vacancy having longer positron lifetime increases. The increase of the experimental positron lifetime with increasing Al composition corresponds to the calculated results showing longer positron lifetime of the Co vacancy than the Al vacancy. However, the absolute values of the theoretical results are larger than the experimental values both at the lowest and at the highest Al composition. The larger lifetime of the calculated values may be attributed to the omission of the lattice relaxation around the vacancy. In CoTi, there is a discrepancy between the experimental and calculated results. Whereas the calculated positron lifetime of the Ti vacancy is longer than the Co vacancy, the opposite trend is observed in the experimental results. In pure metals, it is considered that the inward relaxation occurs around the vacancy. On the other hand, in ionic compounds such as MgO and ZnO, the outward relaxation is induced because of the Coulomb repulsion around the vacancy. In intermetallic compounds, the charge transfer is not so large as in ionic compounds. However, as seen in the CoTi, the charge transfer occurs and it is likely that the charge transfer affects the lattice relaxation around the vacancy. Moreover, the positron trapped at the vacancy may affect the Coulomb repulsion around the vacancy and the magnitude of the lattice relaxation. In order to overcome these problems, the lattice relaxation including the influence of the change in the Coulomb potential by the positron should be introduced in the positron calculation.

4. Conclusions

We have calculated the bulk and vacancy positron lifetimes in intermetallic compounds CoAl and CoTi crystallizing in
the B2 structure based on first-principles electronic structure calculations. In CoAl, the positron lifetime of the Co vacancy is longer than that of the Al vacancy. These calculated positron lifetimes in CoAl can explain the compositional dependence of the experimental positron lifetimes in CoAl. The larger difference in positron lifetime between the Co and Ti vacancies in CoTi is caused by the charge transfer from Ti to Co. The Ti vacancy surrounded by negatively charged Co atoms is more attractive for the positron. The positron wave function is better localized at the more negatively charged environment, which leads to the longer positron lifetime. These results suggest that the positron lifetimes in intermetallic compounds cannot be directly correlated to those of the pure component. When the calculated results for CoTi are compared to the experimental positron lifetimes, the opposite trend is observed. In order to improve the accuracy of the positron lifetime calculation, the lattice relaxation and the change in the Coulomb potential by the positron should be taken into account.

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REFERENCES