

Site preferences of indium impurity atoms in intermetallics having Al_3Ti or Al_3Zr crystal structures

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Abstract Site-fractions of indium impurity probe atoms occupying up to three inequivalent Al-sites in Al_3Ti , Al_3V and Al_3Zr phases were measured using perturbed angular correlation of gamma rays (PAC). Sites were identified via characteristic nuclear quadrupole interactions. Ratios of site-fractions were measured in thermal equilibrium in the range 600 to 1,210 K. Arrhenius plots of the ratios were fitted with thermally activated expressions, yielding differences in vibrational entropies and site-enthalpies. Enthalpy differences were greatest for Al_3Zr , ~ 0.22 eV, and smaller for Al_3Ti and Al_3V , which is correlated with the excess volume of the transition-metal atom over the Al-atom. Vibrational entropy differences were small, in the range 0 to -0.25 k_B .

Keywords Solute atoms · Lattice location · Site preference · Equilibrium sites · Enthalpy of transfer · Vibrational entropy

The site preference of dilute ^{111}In impurities in the Laves phase GdAl_2 was previously studied as a function of composition and temperature [1]. Occupied Gd- and Al-sites were determined through measurements of quadrupole interactions using the method of perturbed angular correlation of gamma rays (PAC). In that study, ^{111}In impurity probe atoms were observed to switch between sites of *different* elements. The ratio of site fractions of indium solutes on Gd- and Al-sites was found to be thermally activated, with solutes transferring from the Gd- to Al-sublattice with increasing temperature. Transfer takes place heuristically through the reaction $\text{In}_{\text{Gd}} + \text{Al}_{\text{Al}} \Leftrightarrow \text{In}_{\text{Al}} + \text{Al}_{\text{Gd}}$, in which Al_{Gd} is an antisite atom that is either created or destroyed. Applying the law of mass action to the reaction leads to $[\text{In}_{\text{Al}}][\text{Al}_{\text{Gd}}]/[\text{In}_{\text{Gd}}] = \exp(-G_{\text{tr}}/k_B T)$, in which G_{tr} is the free energy of transfer

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and in which square brackets represent mole fractions of atoms on the respective sublattices indicated by subscripts. The most useful experimental measure of site preference is the ratio of fractions of probes on the two sites, and, inserting a factor 2 for the 2:1 ratio of sites on the Al and Gd-sublattices, $2f_{\text{Gd}}/f_{\text{Al}} = [\text{In}_{\text{Gd}}]/[\text{In}_{\text{Al}}] = [\text{Al}_{\text{Gd}}] \exp(-G_{\text{tr}}/k_{\text{B}}T)$. Since the site-fraction ratio depends on sample composition through the antisite mole fraction $[\text{Al}_{\text{Gd}}]$, it is not possible to immediately determine the difference of site-enthalpies of In_{Gd} and In_{Al} from an overall fitted activation enthalpy without making additional assumptions or approximations [1].

In this paper, we wish to show that the situation is much simpler for inequivalent sites of the *same* element. The transfer reaction then no longer involves an intrinsic defect such as Al_{Gd} , the site-fraction ratio becomes independent of composition, and the free energy of transfer is directly equal to the difference between enthalpies of the solute atom on the two sites. Measurements were made on Al_3Ti and Al_3V , which have the tetragonal Al_3Ti (DO_{22}) crystal structure, and on Al_3Zr , which has the related tetragonal Al_3Zr (DO_{23}) structure [2]. In both structures, transition-metal (TM) atoms are surrounded by 12 near-neighbor (nn) Al-atoms. There are two inequivalent Al-sites in the Al_3Ti structure, having a 1:2 numerical ratio, and designated Al(1) and Al(2). Site Al(2) has 4 nn TM-atoms in a distorted tetrahedral arrangement and site Al(1) has 4 TM-neighbors in a square arrangement, with the remaining 8 nn sites taken up by Al-atoms. The Al_3Zr structure has three inequivalent Al-sites with equal numbers of atoms. Two sites have locally identical arrangements of neighbor atoms as sites Al(1) and Al(2) in the Al_3Ti structure, and are labeled in the same way, while site Al(3) has four TM-neighbors in a distorted square arrangement. The TM site and sites Al(1) and Al(2) have axially-symmetric electric field gradients (EFG) with principal axes aligned along the tetragonal axes while site Al(3) has an EFG whose principal axis is approximately normal to the tetragonal axis. In previous PAC measurements made for ^{111}In probes in Al_3Ti [3] and in Al_3Zr [4], a signal for only one site was observed which was variously attributed to one of the Al-sites [3] or to the TM-site [3, 4]. However, additional information strongly indicates that the TM-site, at which In probe atoms would be surrounded by 12 Al-atoms, is not occupied due to lack of affinity between atoms of indium and aluminum. Evidence for this lack of affinity includes the following: (a) molten In and Al are immiscible and In and Al have no intermediate phases; (b) the solid solubility of In in pure Al-metal has been measured to be only at the part-per-million level at elevated temperature [5]; (c) an extensive study of site preferences of indium solutes in Ni_2Al_3 phases showed that the solutes prefer to occupy grain-boundary sites rather than to be surrounded by eight Al-atoms in the first neighbor shell [6]. In the present study, point charge calculations were made that suggest that relative EFG's for the sites are very small (TM-site), intermediate in strength (Al(2) site), or twice larger (Al(1) or Al(3) sites).

Samples were made by arc-melting high purity metals under argon with ^{111}In activity (mole fraction $\sim 10^{-8}$). Sample masses were typically 50 mg. Measurements were made using a vacuum oven with pressure lower than 10^{-5} Pa and a four-detector PAC spectrometer. Representative time-domain and Fourier spectra for measurements on Al_3Zr are shown for two temperatures in Fig. 1. For all three phases, one axially symmetric quadrupole interaction signal dominated at low temperature and was attributed to In on the Al(2) site because of the smaller value of its EFG. This signal is illustrated for Al_3Zr at 725 K in Fig. 1, left. It can be seen that amplitudes

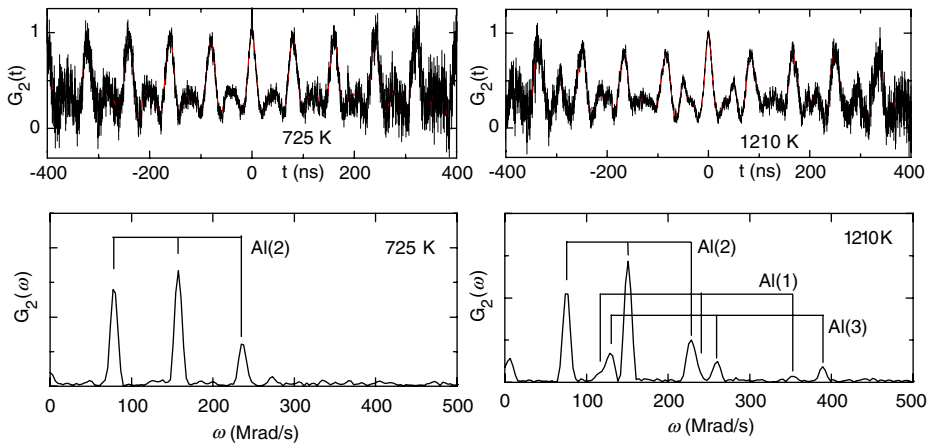
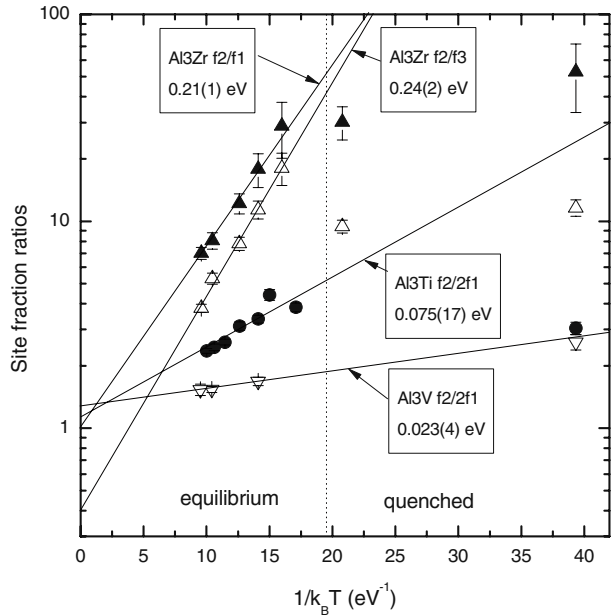


Fig. 1 PAC time-domain and Fourier spectra for ^{111}In probes in Al_3Zr . At 725 K (left) nearly all probes occupy site Al(2) whereas at 1210 K (right) probes also occupy sites Al(1) and Al(3)

of the three frequency components deviate strongly from the proportions 13:10:5 predicted when polycrystalline texture is random. The strong enhancement of the amplitude of the second harmonic is attributed to inhomogeneous crystallization following arc-melting. At high temperature, small site-fractions of additional signals were observed. This is shown in Fig. 1, right, for Al_3Zr at 1,210 K, with two signals that are attributed to indium at sites Al(1) and Al(3). These new signals appeared and disappeared *reversibly* as temperature was increased and reduced. The EFG for site Al(3) in Al_3Zr is not expected to be axially symmetric, but fitted values of the EFG asymmetry parameter η for both new signals were indistinguishable from zero. However, it was possible to identify the signals with sites Al(1) and Al(3) through fits of the amplitudes of the frequency components of each signals. This is because the EFG's for sites Al(1) and Al(2) have parallel axes and therefore must have identical harmonic amplitudes. However, the EFG axis for site Al(3) is oriented in a direction approximately normal to the c -axis and consequently the harmonic amplitudes will differ. One signal was found to have non-random amplitudes very similar to those for Al(2) and was attributed to site Al(1), while the other, which had significantly different amplitudes, was attributed to site Al(3).

Measurements were made on each of the three phases at temperatures up to 1,210 K. Site occupations were observed to be in thermal equilibrium above 600 K. Figure 2 shows Arrhenius plots of ratios of site fractions f_2/f_1 and f_2/f_3 for the three phases, with labels f_n representing site fractions for Al(n) sites. (For the two phases having the Al_3Ti structure, the ratio $f_2/2f_1$ is plotted to account for the factor of 2 difference in the numbers of sites.) Straight lines show results of fits of ratios measured above 600 K to thermally activated expressions of the form $\exp(-G_{\text{tr}}/k_{\text{B}}T) \equiv \exp(\Delta S_{\text{tr}}/k_{\text{B}}) \exp(-\Delta H_{\text{tr}}/k_{\text{B}}T)$, with fitted enthalpy differences given in the figure. The $T = \infty$ intercepts and slopes on the graph give differences in vibrational entropy and enthalpy for each pair of sites. Intercepts at $T = \infty$ show that ΔS_{tr} is very small between sites Al(1) and Al(2), in the range 0 to $-0.25 k_{\text{B}}$. Between sites Al(3) and Al(2), the fitted difference is greater, $\Delta S_{\text{tr}} \cong +0.9 k_{\text{B}}$, suggesting

Fig. 2 Arrhenius plots of ratios of site-fractions of indium solutes on Al(1), Al(2) and Al(3) sites in the indicated phases



a greater number of low-frequency vibrational modes for In on Al(3) sites than on Al(1) or Al(2) sites. However, the different non-random harmonic amplitudes for sites Al(2) and Al(3) make fits of absolute site fractions subject to systematic uncertainty, leading to an uncertain scaling factor for the site fraction ratio f_2/f_3 , unlike for the ratio f_2/f_1 . As a consequence, the enthalpy difference for sites Al(2) and Al(3) is reliable, but not the entropy difference.

Fitted enthalpy differences between indium on site Al(1) or Al(3) and site Al(2) in Al_3Zr were both found to be close to +0.22 eV. Enthalpy differences between indium on site Al(1) and Al(2) were +0.075(17) eV in Al_3Ti and +0.023(4) eV for Al_3V . These differences appear to be correlated with atomic volumes of the TM-atoms. Relative volumes of V/Al/Ti/Zr/In atoms are 0.75:1.00:1.07:1.30:1.46, with the In-probe having the largest volume and creating an outward local strain. Additional strain will occur when the TM atoms are also oversized, and especially for Zr. Strain energy is expected to be more anisotropic, and greater in magnitude, for the “square” configurations of TM-atoms around sites Al(1) and Al(3) than for the tetrahedral configuration around site Al(2). Indeed, the enthalpy differences correlate very well with volume excesses of the TM-metal atoms over Al-atoms.

In summary, PAC has been used to determine differences between enthalpies of indium solutes on inequivalent Al-sites in Al_3Ti and Al_3Zr phases. The only other measurement of enthalpy differences of a solute on inequivalent sites of an element of which we are aware is from a study of indium in the phase Ga_7Pd_3 [7]. Finally, an argument was presented that shows a correlation between observed enthalpy differences and the excess volume of the TM-atoms over Al-atoms.

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