Temperature- and composition-driven changes in site occupation of indium solutes in Gd$_{1+3x}$Al$_{2-3x}$

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Fractional concentrations of indium solutes at Gd sites and Al sites in the Laves phase Gd$_{1+3x}$Al$_{2-3x}$ were measured for different temperatures and sample compositions using perturbed angular correlation spectroscopy. At fixed composition, the fraction of indium on Gd sites was observed to decrease as temperature was increased. At fixed temperature, the fraction of indium on Gd sites was observed to increase as the composition became more deficient in Gd. The trends are explained using a thermodynamic model that couples solute site occupation with concentrations of point defects. The increase in enthalpy of the crystal when indium switches from a Gd site to an Al site was determined to be 0.343(7) eV.

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I. INTRODUCTION

There is considerable interest in the site occupation of solutes in intermetallic compounds because of its effects on many materials properties. Past experiments have shown that a solute may occupy different sites on opposing sides of the stoichiometric composition$^{1-4}$ and that a solute may change sites as a function of temperature.$^{5}$ Such results can be explained if concentrations of solutes on different sites are coupled with concentrations of intrinsic point defects. This is expected, as shown using a thermodynamic model of equilibrium site occupation in binary intermetallic compounds of any structure$^{6}$ results of which have been summarized recently.$^{4,7}$ Features highlighted in Refs. 4 and 7 have been noted in earlier simulations of solute site occupation carried out for NiAl,$^8$ TiAl,$^9$ and Ni$_3$Al.$^{10,11}$ In the present work, changes in site occupation of indium solutes in GdAl$_2$ were measured as a function of both composition and temperature using perturbed angular correlation of gamma rays (PAC) and analyzed using a thermodynamic model.

PAC is an attractive experimental technique for investigation of solute site occupation because it requires only very low concentrations of probes, used as solutes, which simplifies the thermodynamic analysis. Using PAC, characteristic interactions between the solute’s nuclear quadrupole moment and electric field gradients (EFGs) in the crystal are used to determine the crystallographic locations of the solutes in some structures.

The EFG at a nucleus is the second derivative of the electrostatic potential due to the extranuclear charges in the surrounding crystal. The EFG is a traceless, second-order tensor $V_{ij}$, which in diagonal form has components customarily ordered so that $|V_{zz}| \geq |V_{xy}| \geq |V_{xx}|$. The two independent parameters usually reported are the principal component $V_{zz}$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. For nuclei at a site with cubic site symmetry, the EFG is zero ($V_{zz} = 0$ and $\eta = 0$). For sites with a threefold axis of symmetry (for example, $3m$ site symmetry), $V_{zz} \neq 0$ and $\eta = 0$. For lower symmetry, $V_{zz} \neq 0$ and $0 < \eta \leq 1$. $V_{zz}$ and $\eta$ can be used to distinguish sites and provide limited information about point symmetries of the sites.

Changes in solute site occupation have been observed using PAC in previous studies. Indium solute site occupation was found to vary as a function of composition in Ni$_3$Ga$_3$ and other phases having the Ni$_2$Al$_3$ structure.$^{3,4}$ Site occupation of indium was observed to change as a function of temperature in HfAl$_2$.$^5$ Changes in site occupation of hafnium with temperature were observed in LiNbO$_3$ and LiTaO$_3$, and the changes were analyzed using a thermodynamic model coupled to intrinsic defects.$^{12}$

The present study in GdAl$_3$ demonstrates changes in site occupation of indium as functions of both composition and temperature. GdAl$_2$ is a cubic Laves phase having the Cu$_2$Mg (C15) structure.$^{13}$ It has several features that suggested one might observe changes in site occupation by indium solutes. First, one can easily distinguish the two sites using PAC because the Gd site has $3m$ (cubic) site symmetry while the Al site has $3m$ (axial) site symmetry. Second, indium is isovalent with Gd and Al, suggesting that it would not have a strong chemical preference for either site. Third, the atomic volume of In is intermediate between volumes of Gd and Al, suggesting that there would not be a large difference in strain energy if In were to substitute at one site versus the other.

GdAl$_3$ is thought to disorder by formation of thermally activated “quadruple defects,” comprised of three aluminum vacancies ($V_{Al}$) and one aluminum antisite (Al$_{Gd}$).$^{14}$ These were the defects observed using x-ray diffraction, ac magnetic susceptibility, and dc magnetization after high-energy ball milling.$^{14}$ The formation energy of quadruple defect disorder was estimated to be 0.57 eV per defect and to be lowest of all types of disorder using Miedema’s semiempirical model.$^{15}$ GdAl$_3$ appears as a line compound in the Gd–Al phase diagram, however, as for all compounds, its phase field must have a finite, though possibly very small, width. Therefore, the compound is better represented by the formula Gd$_{1+3x}$Al$_{2-3x}$, in which $x$ denotes the deviation from the stoichiometric composition. Since formation enthalpies of the neighboring GdAl$_3$ and GdAl phases at room temperature are both higher than that of Gd$_{1+3x}$Al$_{2-3x}$, the phase field of Gd$_{1+3x}$Al$_{2-3x}$ should extend to both sides of the stoichiometric composition. This suggested to us that we...
could prepare Gd$_{1+x}$Al$_{2-x}$ samples with Gd-poor and Gd-rich compositions and study solute site occupation as a function of composition as well as temperature.

II. EXPERIMENTAL METHODS

A. Sample preparation

Gd-Al samples with compositions between about 25.7 at. % Gd and 34.0 at. % Gd were prepared by arc melting 99.9% Gd foil and 99.997% Al foil with carrier-free $^{111}$In under Ar atmosphere. Indium concentrations were very dilute (about $10^{-7}$ at. %). Samples were annealed at 1273 K for 2–4 h either in vacuum better than $10^{-6}$ mbar or in flowing 99.9995% H$_2$ before measurement to anneal out excess defects and increase grain size. Observed PAC signals and site occupation behavior did not appear to depend on annealing treatment. PAC signals exhibited only small frequency distributions, which indicated that the treatments resulted in well crystallized and ordered crystals having low concentrations of point defects.

Samples labeled A through F were prepared with nominal compositions of 32.5, 33.3, 33.5, 33.3, 34.3, and 33.7 at. % Gd. Typically, about 0.1 mg was lost out of a total mass of about 35 mg during each melt, and uncertainties in compositions of the melted samples were determined by assuming that decreases in mass were due entirely to loss of one element or the other. Samples C and E gained 0.15 mg during anneals in H$_2$, which is attributed to oxidation of Gd by impurity oxygen in the hydrogen.\textsuperscript{19} Compositions of those two samples were adjusted according to the amounts of Gd lost from the intermetallic phase. Considering the above effects, best estimates for compositions of samples A through F as measured are 32.5±0.2, 33.3±0.2, 32.7±0.3, 33.3±0.2, 33.5±0.1, and 33.7±0.3 at. % Gd. The width of the Gd$_{1+x}$Al$_{2-x}$ phase field, which has not been determined, may be so narrow that some samples were in two-phase fields, containing small volume fractions of neighboring phases. A GdAl$_3$ sample [25.7(1) at. % Gd] was therefore prepared to check if any signals observed in the present work were from that compound.

B. Perturbed angular correlation spectroscopy

Crystallographic locations of indium were identified using gamma radiation emitted from $^{111}$In/Cd probes dissolved in Gd$_{1+x}$Al$_{2-x}$. $^{111}$In decays to the second excited state of $^{111}$Cd via electron capture. The Cd nucleus subsequently decays to its ground state by emitting two gamma rays in succession. The intermediate 247 keV level has spin $5/2^+$ and a long lifetime, $\tau=120$ ns. For such a cascade, there is an anisotropic probability of detecting the second gamma ray of the cascade with respect to the first gamma ray’s direction of detection. When an EFG is present at the Cd nucleus, the system is perturbed and populations of the magnetic substates of the 247 keV level evolve over the lifetime of the level. As a result, there is a time dependence in the angular correlation between the gamma rays of the cascade that is characterized by a perturbation function $G_2(t)$.

The time evolution of the magnetic substates is analogous to spin precession in a magnetic field. For a spin-5/2 nuclear quadrupole interaction, there are three interaction frequencies $\omega_1$, $\omega_2$, and $\omega_3=\omega_1+\omega_2$, which are functions of the magnitude of electric field gradient $V_{zz}$ and $\eta$.\textsuperscript{20} For $\eta=0$, the frequencies are $\omega_i=3eQV_{zz}/2\hbar$ where $Q$ is the quadrupole moment of the nucleus, $\omega_2=2\omega_1$, and $\omega_3=3\omega_1$. When EFG axes are randomly oriented, as for polycrystalline samples such as the Gd$_{1+x}$Al$_{2-x}$, samples of this study, the perturbation function is

$$G_2(\omega_1, \eta, \sigma, t) = s_0 + \sum_{n=1}^{3} s_n \cos(\omega_n t) \exp \left( -\frac{1}{2} (\sigma \omega_n t/\omega_1) \right).$$

(1)

In general, the amplitudes $s_n$ are functions of $\eta$. For most signals observed in this study, $\eta=0$, in which case $s_0=1/5$, $s_1=13/35$, $s_2=2/7$, and $s_3=1/7$.\textsuperscript{20} The exponential factors account for inhomogeneous broadening due to distant defects or lattice strains.

When nuclei are located in more than one crystallographic environment, the overall perturbation function is a superposition of individual functions,

$$G_2(t) = \sum_i f_i G_2(\omega_{1,i}, \eta, \sigma, t),$$

(2)

in which the signal amplitude $f_i$ is the fraction of nuclei in site $i$. The hyperfine parameters $\omega_{1,i}$ and $\eta$ identify the crystallographic site, and the site fractions $f_i$ are direct measures of site occupation. While hyperfine interactions are measured in the 247 keV level of Cd, the site fractions are determined by the equilibrium distribution of In, since there is not enough time after the decay of In for Cd to jump to a different site. Hyperfine parameters and site fractions were determined by least squares fits of Eqs. (1) and (2) to experimental spectra.

Data were collected using a PAC spectrometer with four fixed BaF$_2$ scintillation detectors separated by 90° in a plane. Measurements at elevated temperature were made in vacuum better than $10^{-6}$ mbar in a furnace designed to minimize sample-detector distance.\textsuperscript{21} The spectrometer used a slow–fast coincidence counting method with “nongated” timing signals.\textsuperscript{22} Data reduction took into account correlated absorption of gamma rays in the source, which primarily leads to a vertical offset in the perturbation function,\textsuperscript{23–25} and attenuation at high count rates.\textsuperscript{22} These artifacts were removed from all spectra prior to analysis, and only corrected spectra are shown. A detailed description of the data reduction methodology can be found in Ref. 22.

III. RESULTS

PAC spectra for four Gd$_{1+x}$Al$_{2-x}$ samples measured at 823 K are shown in Fig. 1. The spectrum for sample $F$ [Fig. 1(a)] exhibits only one quadrupole interaction signal with fundamental frequency $\omega_1=45$ Mrad/s. The spectrum for sample $D$ [Fig. 1(b)] exhibits, in addition to the 45 Mrad/s signal, a 0 Mrad/s signal visible as a small vertical offset. In the spectrum for sample $B$ [Fig. 1(c)], the site fraction of the...
GdAl$_3$ has the Ni$_3$Sn structure, in which the Gd site has 6
trum, shown in Fig. 2, exhibits only a single signal with
or 14 Mrad/s signals originate from that phase. The spec-
signals observed in GdAl$_2$. It is worth noting that this im-

45 Mrad/s signal is half replaced by two signals: the 0
Mrad/s signal and an 8 Mrad/s signal. Finally, the spectrum
for sample A [Fig. 1(d)] exhibits the smallest site fraction of
the 45 Mrad/s signal, accompanied by 0 Mrad/s, 8 Mrad/s,
and 14 Mrad/s signals. The site fractions in the samples are
 correlated with composition: the site fraction of the 45
Mrad/s signal is highest for sample F, which is Gd poor, and the
signal was not observed for sample F, which is Gd rich.
Thus, the site fraction of the 0 Mrad/s signal increases with
decreasing Gd content, whereas the site fraction of the 45
Mrad/s signal decreases with decreasing Gd content.

The site fraction of the 8 Mrad/s signal, like that of the 0
Mrad/s signal, was observed to increase with decreasing Gd
content. Because the concentration of structural defects for
Gd-poor compositions also increases as Gd-content de-
creases, the 8 Mrad/s most likely arises from probes that
have a nearby structural defect. Possible structural defects
are the Al antisite defect Al$_{Gd}$ or the Gd vacancy $V_{Gd}$, both
located on the Gd sublattice.

The low frequency of the 8 Mrad/s signal indicates that it
originates from probes on Gd sites and not on Al sites, as
follows. Typical interaction frequencies for Cd probes at cu-
bic sites in other metallic systems with a defect in a nearest
neighbor site are in the range of 50 to 100 Mrad/s,\textsuperscript{30} signifi-
cantly higher than 8 Mrad/s. A small EFG with a corre-

FIG. 2. PAC spectrum of $^{111}$In/Cd in GdAl$_3$ measured at room
temperature.
sample A. Because sample A was the most Gd poor of all samples, it is reasonable to conclude that, like the 8 Mrad/s signal, the signal also involves the Gd-poor structural defect. One possibility is that the 14 Mrad/s signal arises from multiple Al Gd defects near Cd Gd probes, in analogy with multiple vacancy configurations that have been detected around probes in B2 compounds.\(^3\)\(^1\)–\(^3\)\(^3\) However, it was not possible to identify the 14 Mrad/s signal more positively.

In Fig. 3, representative PAC spectra collected for sample C at different temperatures are shown. The site fraction of the 0 Mrad/s signal, visible as a vertical offset in each spectrum, can be seen to decrease with increasing temperature with a compensating increase in the fraction of the signal with frequency of about 45 Mrad/s. This trend shows that indium tends to occupy Gd sites at low temperature and Al sites at high temperature.

It is evident in Fig. 3 that the frequency of the signal for Cd on the Al site decreases with increasing temperature, which is attributed in part to thermal expansion. Figure 4 shows a plot of the temperature dependence of the frequency \(\omega_1\) for all samples, in which it can be seen that the frequencies for different samples overlap excellently. A linear fit of data for all samples (excluding sample A, which had larger errors) yielded \(\omega_1 = 48.8(3)\) Mrad/s at room temperature and \(d\omega_1/dT = -0.0109(3)\) Mrad/s/K. Below, this signal is labeled the 49 Mrad/s signal, in reference to its frequency at room temperature. Hyperfine parameters and site attributions of all signals are summarized in Table I.

Major conclusions from the above discussion are that the site fraction of the 0 Mrad/s signal \(f_0\) corresponds to \(f_{Gd}\), the fraction of probes on Gd sites without nearby defects, and that the site fraction of the 49 Mrad/s signal \(f_{49}\) corresponds to \(f_{Al}\), the fraction of probes on Al sites. For analysis using a thermodynamic model, it is useful to make an Arrhenius plot of \(f_0/f_{49}\), shown in Fig. 5 for samples A–E. (The ratios of site fractions for sample F were consistent with zero in all measurements and are not visible in the figure.) As can be seen, indium tends to occupy Gd sites at low temperature and Al sites at high temperature in each of the five samples.

The temperature dependences of the site fractions of the 8 Mrad/s signal \(f_8\), attributed to a probe on a Gd site with a nearby defect, and of the 0 Mrad/s signal \(f_0\), attributed to a probe on a Gd site without a nearby defect, can in principle be used to determine the interaction energy between the probe and defect. For this, it is useful to construct an Arrhenius plot of the ratio \(f_8/f_0\), shown in Fig. 6 for samples B and C (ratios for other samples had large scatter). The ratios can be seen to increase as the temperature decreases, indicating an attractive interaction between the Gd-poor structural defect and the indium probe.

IV. THERMODYNAMIC ANALYSIS OF SITE OCCUPATION

A thermodynamic model was employed to interpret the temperature and composition dependence of the data in Fig. 5 (see Appendix). The model links indium concentrations on each sublattice of Gd\(_{1+3}\), Al\(_{2-3}\) to the concentrations of intrinsic defects. Defects are assumed to be present only in small concentrations and to be noninteracting. The effect of interaction between In\(_{Gd}\) and the structural defect of Gd-poor compositions is considered separately in the next section. In accordance with conclusions of Bakker and co-workers,\(^1\)\(^4\)\(^,\)\(^1\)\(^5\) the dominant defects are assumed to be Al\(_{Gd}\) and V\(_{Al}\), and other defect concentrations were neglected.

One way to link changes in indium site occupation to intrinsic defects is via the reaction

\[
\text{In}_{Gd} + \text{Al}_{Al} \rightarrow \text{In}_{Al} + \text{Al}_{Gd},
\]

which describes the partitioning of indium between Al and Gd sites in equilibrium. Application of the law of mass action to Eq. (3) relates the ratio of indium concentrations on each site to the Al\(_{Gd}\) concentration via
The ratio of site fractions is defined in terms of solute concentrations as $f_0/f_{49} = f_{Gd}/f_{Al} = \frac{[Al_{Gd}]/[Al]}{[In_{Gd}]/[In]}$, in which the factor 1/2 is the ratio of the numbers of sites on the Gd and Al sublattices. Using this expression in conjunction with Eq. (4), one obtains for the ratio of site fractions

$$f_0/f_{49} = \frac{[Al_{Gd}]}{[In_{Gd}]}\exp(-S_{xfer}/k_B T)$$

Thus, the site fraction ratio is directly proportional to the concentration of $Al_{Gd}$. The temperature and composition dependence of $[Al_{Gd}]$ and consequent behavior of the site fraction ratio are discussed in the Appendix.

Below approximately 673 K, the ratios in Fig. 5 are independent of temperature, indicating that the samples were unable to establish equilibrium through defect motion on the time scale of the measurements. At and above 673 K, the ratios of site fractions exhibit reversible, activated behavior. The slopes of the data in Fig. 5 are similar for samples $A$–$E$,

indicating samples $B$–$E$ are also Gd poor like sample $A$; however, the samples have different compositions as indicated by offsets in ratios for the samples. Up to the highest measured temperature, 1473 K, there is no clear evidence of curvature in the ratios, which would have indicated formation of thermally activated defects. Based on these observations we conclude that the samples were sufficiently Gd poor for structural $Al_{Gd}$ to dominate over any thermally activated $Al_{Gd}$, in which case $[Al_{Gd}] \approx -3x$ (see the Appendix). Hence, the data in Fig. 5 can be interpreted using

$$f_0/f_{49} = -\frac{3x}{2}\exp(-S_{xfer}/k_B T)$$

and the temperature dependence of $f_0/f_{49}$ is due entirely to the Boltzmann factor involving $H_{xfer}$.

For samples $A$, $B$, $C$, $D$, and $E$ were fitted to Eq. (6), with results shown by lines in Fig. 5. Values for $H_{xfer}$, obtained from the slopes, and for the products $-\frac{3x}{2}\exp(-S_{xfer}/k_B T)$, obtained from the intercepts at $1/k_B T = 0$, are listed in Table II. $H_{xfer}$ is an intrinsic property of the transfer process and therefore should be the same for all samples. The average value is $H_{xfer} = 0.343(7) \text{ eV}$. $S_{xfer}$ should also be the same for all samples; thus, in principle one can determine $S_{xfer}$ from the fitted intercepts using the deviations from stoichiometry. Unfortunately, the large uncertainties of the compositions of the samples do not allow a meaningful determination of $S_{xfer}$ to be made.

One can, however, determine the relative deviations from stoichiometry for sample $A$–$E$. For example, one could take ratios of the fitted intercepts to obtain the relative deviations from stoichiometry for samples $A$–$E$. A more accurate determination was made by using the actual $f_0/f_{49}$ data rather than the fitted intercepts. Because the range of probable composition for sample $A$ was entirely Gd poor, the deviations from stoichiometry for the other samples were found relative to that of sample $A$. The ratio of deviation from stoichiometry of sample $n$ to that of sample $A$ was determined using the corresponding site fraction ratio at a given temperature; that is,

$$\frac{x_n}{x_A} = \frac{(f_0/f_{49})_{\text{sample } n}}{(f_0/f_{49})_{\text{sample } A}}$$

Ratios $x_n/x_A$ were calculated from all available pairs of $f_0/f_{49}$ for temperatures at which samples $n$ and $A$ were both measured and then averaged for each sample, yielding $x_B/x_A = 0.75(13)$, $x_C/x_A = 0.42(9)$, $x_D/x_A = 0.26(5)$, and $x_E/x_A = 0.10(2)$.

![Figure 5](image-url)
In Gd probe can be determined from the ratio of the 0 Mrad/s thermal defect, the interaction enthalpy between Al Gd and the aluminum, as Gd content decreases.

To illustrate more clearly changes in site occupation as a function of composition, fractions of probes on Al sites are plotted in Fig. 7 versus the relative deviation from stoichiometry \(x/|x_A|\) for several temperatures. For each temperature, the Al-site fraction decreases as the magnitude in the deviation from stoichiometry increases. Overall changes in site fractions from a composition near the stoichiometric average value are as large as 80\% at low temperatures (at and below 673 K), decreasing to about 20\% in measurements at high temperatures (1073 and 1173 K). Based on the nominal composition of sample A, these changes take place over a composition range of roughly 0.8 at.\% Gd. The changes are consistent with heuristic rules identified from a more extensive examination of the thermodynamic model of site occupation, including simulations.\(^4\)\(^6\)\(^7\) In particular, a solute tends to occupy the lattice site of an element in which a compound is deficient. This is seen in Fig. 7 as a decrease in \(f_{A1}\), which corresponds to an increase in occupation of Gd sites by indium, as Gd content decreases.

V. THERMODYNAMIC ANALYSIS OF DEFECT ASSOCIATION

Assuming for concreteness that \(\text{Al}_{\text{Gd}}\) is the Gd-poor structural defect, the interaction enthalpy between Al Gd and the In Gd probe can be determined from the ratio of the 0 Mrad/s and 8 Mrad/s site fractions. Since the concentration of \(\text{Al}_{\text{Gd}}\) is small, one can write the reaction for binding (or disassociation) as

\[
\{\text{In}_{\text{Gd}} : \text{Al}_{\text{Gd}}\} \rightleftharpoons \text{In}_{\text{Gd}} + \text{Al}_{\text{Gd}},
\]

in which \(\{\text{In}_{\text{Gd}} : \text{Al}_{\text{Gd}}\}\) denotes a bound pair of defects. Using the law of mass action, the concentrations of defects in Eq. (8) are related according to

\[
\frac{[\text{In}_{\text{Gd}}][\text{Al}_{\text{Gd}}]}{[\text{In}_{\text{Gd}} : \text{Al}_{\text{Gd}}]} = \exp(-G_B/k_B T),
\]

in which the free energy of binding is \(G_B = H_B - T S_B\) and \(z = 4\) is the number of neighboring Gd sites closest to a Gd site. \(H_B > 0\) indicates an attraction between neighboring defects. The ratio of the site fractions \(f_{8}/f_{0}\) is equal to the ratio of concentrations of bound and unbound indium probes on Gd sites: \([\text{In}_{\text{Gd}} : \text{Al}_{\text{Gd}}]/[\text{In}_{\text{Gd}}]\). Since the concentration \([\text{Al}_{\text{Gd}}]\) was found to be independent of temperature for each sample and equal to \(-3x\), one has the following relation between the site fraction ratio and temperature:

\[
f_{8}/f_{0} = -12x \exp(-S_B/k_B) \exp(+H_B/k_BT).
\]

VI. DISCUSSION

Qualitative trends of indium site occupation in Gd\(_{1+3x}\)Al\(_{1-3x}\) are independent of the actual structural defect that is dominant in Gd-poor samples. One can readily recast the site-occupation model under the assumption that \(V_{\text{Gd}}\) is the dominant structural defect in Gd-poor samples, leading to

![FIG. 7. The fraction of solutes occupying Al sites (with frequency 49 Mrad/s) for samples A–E, plotted versus relative deviation from stoichiometry \(x/|x_A|\) at the indicated temperatures.](image_url)
\[ f_{\text{Gd}}/f_{\text{Al}} = \frac{1}{2} \left( \frac{V_{\text{Gd}}}{V_{\text{Al}}} \right)^{3/2} \exp \left( -S_{\text{Xfer}}/k_B \right) \exp \left( H_{\text{Xfer}}/k_B T \right), \]

with \( V_{\text{Gd}} = -9x/2 \) for Gd-poor compositions in which there is little thermal activation of V\text{Gd} defects. The physical interpretation to be given to the activation enthalpy \( H_{\text{Xfer}} = 0.343(7) \text{ eV} \) would differ, with \( H_{\text{Xfer}} = h_{\text{Al}}^{\text{In}} - h_{\text{Gd}}^{\text{In}} + \frac{1}{2} h_{\text{Gd}}^{\text{Al}} \) instead of \( H_{\text{Xfer}} = h_{\text{Al}}^{\text{In}} - h_{\text{Gd}}^{\text{In}} + h_{\text{Gd}}^{\text{Al}} \). Similarly, interpretation of the data for defect association between indium and the Gd-poor defect would be affected by a different identity for the Gd-poor structural defect, but the \( H_{\text{Xfer}} = 0.12(6) \text{ eV} \) would remain the same. Quantitatively, relative deviations from stoichiometry \( x_A / x_A \) would differ because of the 3/2-power dependence on \( V_{\text{Gd}} \).

### VII. SUMMARY AND CONCLUSION

Fractional concentrations of indium solutes at Gd and Al sites in Gd\(_{1+3x}\)Al\(_{2-3x}\) were measured as a function of temperature and composition using perturbed angular correlation spectroscopy. The fraction at Al sites was found to increase with either increasing temperature or Gd content. The transfer of an indium solute from the gadolinium to aluminum sublattice was found to increase the enthalpy of the crystal by 0.343(7) eV. In addition, indium solutes on Gd sites were found to have an attractive interaction with the Gd-poor structural defect, with a binding enthalpy of 0.12(6) eV.

Indium was observed to switch almost completely from Gd to Al sites in response to changes in temperature of order 400 K or changes in composition of order 0.8 at. % Gd. Similarly large changes in solute site occupation may occur in other compounds and significantly influence material properties. Without thorough investigation of site occupation as a function of composition and temperature, one risks an incomplete assessment of site preference behavior, such as identification of one preferred site to the exclusion of other sites. Many phases that appear as line compounds in binary phase diagrams are likely to have widths of phase fields comparable to that of GdAl\(_2\), so that composition dependences may be as great as in the present study. At a minimum, one should investigate a reported line compound by preparing samples to be rich or poor in each element in order to observe site preferences at the opposing boundary compositions.

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### APPENDIX

Equilibrium concentrations of intrinsic defects and solutes on the various sublattices of a crystal can be determined by minimizing the Gibbs free energy of the crystal subject to structural and compositional constraints within the framework of a canonical ensemble. This method is used below to determine the composition and temperature dependence of indium solute site occupation and intrinsic defect concentrations in Gd\(_{1+3x}\)Al\(_{2-3x}\). For simplicity, it is assumed that only V\text{Al} and Al\text{Gd} defects are present in significant concentrations, although the following analysis is easily generalized to include V\text{Gd} and GdAl\(_2\) defects. It is assumed also that indium does not dissolve interstitially. It is assumed further that defect concentrations are small and that defects do not interact.

Numbers of defect and nondefect species will be indicated below by \( x^\gamma y^\nu \) in which \( x \) denotes the species (Al, Gd, In or V for vacancy) and \( y \) denotes the sublattice or site. \( N^X \) denotes the total number of atoms or vacancies \( X \), and \( N^y \) the total number of sites of sublattice \( y \). Using \( N \) to represent the total number of unit cells, the free energy of the crystal can be written as

\[ G = N g_0 + N_{\text{Gd}}^{\text{Al}} h_{\text{Al}}^{\text{Gd}} + N_{\text{Al}}^{\text{V}} h_{\text{Al}}^{\text{V}} + N_{\text{Gd}}^{\text{In}} h_{\text{Gd}}^{\text{In}} + N_{\text{Al}}^{\text{In}} h_{\text{Al}}^{\text{In}} - kT \ln \Omega, \]

in which \( g_0 \) is the Gibbs free energy of the crystal per unit cell in the absence of defects. \( h^\gamma x^\nu \) is the free energy of defect \( X \) on sublattice \( y \), and \( \Omega \) the number of possible ways to arrange the defects,

\[ \Omega = \frac{N_{\text{Al}}! N_{\text{Gd}}!}{N_{\text{Al}}^{\text{Gd}} N_{\text{Al}}^{\text{V}} N_{\text{Gd}}^{\text{V}} N_{\text{Gd}}^{\text{In}} N_{\text{Al}}^{\text{In}}}. \]

The free energy of a defect \( h^\gamma x^\nu \) is defined as the difference between the free energy of a crystal containing one defect \( X \), and the perfect crystal at temperature \( T \), for which \( h^\gamma x^\nu \) is the difference in enthalpy and \( s^\gamma x^\nu \) is the difference in vibrational entropy.

When minimizing the Gibbs free energy with respect to the \( N \)'s that appear in the above equations, the \( N \)'s cannot be varied independently. First, the composition of the compound dictates that the ratio of numbers of Gd and Al atoms satisfies

\[ N_{\text{Gd}}^{\text{Gd}} = \frac{N_{\text{Gd}}^{\text{Gd}}}{N_{\text{Al}}^{\text{Al}} + N_{\text{Gd}}^{\text{Gd}}} = \frac{1 + 3x}{2 - 3x} \]  \hspace{1cm} (A3)

Second, the numbers of sublattice sites must satisfy \( 2N_{\text{Gd}} = N_{\text{Al}} \), so that

\[ 2N_{\text{Gd}}^{\text{Gd}} + 2N_{\text{Gd}}^{\text{Al}} + 2N_{\text{Gd}}^{\text{V}} = N_{\text{Al}}^{\text{Al}} + N_{\text{Al}}^{\text{V}} + N_{\text{Al}}^{\text{In}}. \]

(A4)

Since indium concentrations were negligible in the PAC experiments, we neglect the numbers of In atoms in Eq. (A4) to obtain a simpler equation of constraint,

\[ 2N_{\text{Gd}}^{\text{Gd}} + 2N_{\text{Gd}}^{\text{Al}} = N_{\text{Al}}^{\text{Al}} + N_{\text{Al}}^{\text{V}}. \]

(A5)

Finally, the choice of a canonical ensemble requires that the numbers of Gd and Al atoms be fixed. For the defect model assumed here, Gd atoms are found only on the Gd sublattice, so that a third constraint can be expressed simply as

\[ N_{\text{Gd}} - N_{\text{Gd}} = 0. \]

(A6)

Equation (A3) in conjunction with Eq. (A6) constrains the number of Al atoms.

With the above three constraints [Eqs. (A3), (A5), and (A6)], one can obtain the conditions of equilibrium using the Lagrange method of undetermined multipliers. A system of
In the dilute defect concentration limit, \([\text{Al}_{\text{Gd}}]=1\) may be inserted into Eq. (A7), and the resulting equation can be substituted into Eq. (A11) to rewrite it in terms of a fourth order polynomial in \([\text{Al}_{\text{Gd}}]^{1/3}\):

\[
[\text{Al}_{\text{Gd}}]^{4/3} + 3x[\text{Al}_{\text{Gd}}]^{1/3} - (\frac{2}{3} + 2x)K_4^{1/3} = 0. \tag{A12}
\]

Equation (A12) can be solved numerically to determine the \(\text{Al}_{\text{Gd}}\) concentration for given values of \(x, H_4,\) and \(S_4\).

According to Eq. (A12), \(\text{Al}_{\text{Gd}}\) is the "structural" defect that must be present at 0 K and for \(x<0\) in order to accommodate the deviation from stoichiometry while preserving the crystal structure. It is useful to examine how its concentration changes with temperature and composition. At the stoichiometric composition, \(x=0\), there are no structural defects and \(\text{Al}_{\text{Gd}}\) defects are formed solely by thermal activation; from Eq. (A12), \([\text{Al}_{\text{Gd}}]=(2/3)^{1/3}K_4^{1/3}\). For nonstoichiometric compositions at a sufficiently high temperature that the majority of \(\text{Al}_{\text{Gd}}\) defects are thermally activated, the solution is still approximately \([\text{Al}_{\text{Gd}}]=(2/9)x^{1/3}K_4^{1/3}\). At low temperatures, the behavior of \([\text{Al}_{\text{Gd}}]\) differs significantly on either side of stoichiometry. For \(x<0\), \([\text{Al}_{\text{Gd}}]^{-3x}\). For \(x>0\), \(\text{Al}_{\text{Gd}}\) defects are only thermally activated and compensate \(\text{V}_{\text{Al}}\) defects (\(\text{V}_{\text{Al}}\) is the structural defect for \(x<0\), \([\text{Al}_{\text{Gd}}]=3[\text{Al}_{\text{Gd}}]^{1/3}\)). The unit cell energy \(g_0\) appears in (A7) because the right-hand side of reaction (A8) includes one more unit cell than the left-hand side.

A second equation that relates defect concentrations to energies is

\[
\frac{[\text{In}_{\text{Al}}][\text{Al}_{\text{Gd}}]}{[\text{In}_{\text{Gd}}][\text{Al}_{\text{Al}}]} = \exp\left(-\frac{\ln[\text{In}_{\text{Al}}] - \ln[\text{In}_{\text{Gd}}] + \ln[\text{Al}_{\text{Al}}]}{k_BT}\right) = \exp\left(-\frac{G_{\text{sfer}}}{k_BT}\right), \tag{A9}
\]

which describes equilibration of indium solutes between Gd and Al sublattices and can be represented by

\[
[\text{In}_{\text{Gd}}] + [\text{Al}_{\text{Al}}] = [\text{In}_{\text{Al}}] + [\text{Al}_{\text{Gd}}]. \tag{A10}
\]

In Eq. (A9), \(G_{\text{sfer}}=H_{\text{sfer}}-TS_{\text{sfer}}\) is the change in free energy of the crystal when indium changes sites, including a change in enthalpy \(H_{\text{sfer}}\) and a change in vibrational entropy \(S_{\text{sfer}}\).

Defect concentrations can be obtained by first rewriting Eq. (A3) in terms of fractional concentrations and by substituting \([\text{Al}_{\text{Al}}]=1-[\text{V}_{\text{Al}}]\) to obtain

\[
3[\text{Al}_{\text{Gd}}] + 9x = (2 + 6x)[\text{V}_{\text{Al}}]. \tag{A11}
\]
For a nonstoichiometric composition, point defects must be present in order to preserve the correct ratio of lattice sites and maintain a single phase. These defects are referred to as structural defects, and their concentrations increase with the magnitude of the deviation from stoichiometry.


