LATTICE LOCATIONS AND DIFFUSION IN INTERMETALLIC COMPOUNDS EXPLORED THROUGH PAC MEASUREMENTS AND DFT CALCULATIONS

By

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LATTICE LOCATIONS AND DIFFUSION IN INTERMETALLIC COMPOUNDS EXPLORED THROUGH PAC MEASUREMENTS AND DFT CALCULATIONS

Abstract

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Site preferences of $^{111}$In/Cd impurity probe atoms were studied as a function of composition in Al$_3$Ni and as a function of temperature in Al$_3$Ti and Al$_3$Zr structures using perturbed angular correlation of gamma rays (PAC). Spectra for Ni-rich Al$_3$Ni exhibit a prominent quadrupole interaction (QI) signal attributed to one of two Al-sites. For Ni-poor samples, spectra exhibited an ill-defined QI attributed to probes located in grain boundaries. Al$_3$Ti and Al$_3$Zr structures have one TM-site and several Al-sites. At low temperature, probes were determined to occupy an Al-site that has the same local atomic coordination. At higher temperature, probes were observed to transfer partially to other Al-sites. Enthalpy differences of indium solutes at the different sites were determined from equilibrium measurements of ratios of site fractions as a function of temperature.

To provide additional insight, energies of In-solutes and electric field gradients (EFG) at nuclei of daughter $^{111}$Cd-solutes were calculated using density functional theory.
(DFT). It was found for all systems that EFG calculations were not adequate to unambiguously identify the sites occupied. However, site energy calculations helped to identify the sites occupied in all systems studied. Calculated site energy differences are in good agreement with measurements.

In separate work, jump frequencies of probes were earlier measured at high temperature using PAC for $\text{In}_3R$ ($R =$ rare-earth) having the $L1_2$ structure [Phys. Rev. Lett., 102, 2009]. In that work, comparison of measurements made for samples that were In-rich and In-poor led to the conclusion that the dominant diffusion mechanism involves $R$-vacancies in light lanthanide-indides (such as $\text{In}_3\text{La}$) and In-vacancies in heavy lanthanide-indides (such as $\text{In}_3\text{Lu}$). DFT calculations were carried out to determine whether the observations could be explained by gradual changes in energies of In- and $R$-vacancies along the $\text{In}_3R$ series. Instead, calculations showed the opposite behavior: More In-vacancies in $\text{In}_3\text{La}$ and more $R$-vacancies in $\text{In}_3\text{Lu}$. This unexpected result indicates that other factors control diffusion behavior, such as differences in migration enthalpies leading to large changes in jump frequencies.
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Chapter 1: Introduction

In this work, perturbed angular correlation (PAC) spectroscopy and density functional theory (DFT) were employed to study atomic movements and site preferences of solutes in intermetallic compounds. Understanding site preferences and diffusion of solutes contributes to understanding the physical properties of ordered compounds. Intermetallic compounds have been studied, among other purposes, for potential use as structural materials under different loading conditions, temperatures and environments [1, 2]. Mechanical properties of intermetallic compounds can be improved by the addition of ternary elements [3, 4]. For ordered intermetallic compounds, as opposed to disordered alloys, substitutional impurities may exhibit significant site preferences [5-8]. Information of the site occupation of substitutional elements in intermetallic compounds is particularly useful in controlling the mechanical properties [9].

There is recent interest in diffusion mechanisms in compounds having increasingly complex structures [10]. Most commonly, diffusion is mediated by atomic vacancies when structures are close-packed and atomic sizes of the different elements are similar. In highly-ordered compounds, for which the energy cost to make an antisite atom or vacancy defect is large, atom movement can occur only in correlated jump sequences that eliminate any lattice disorder produced by jumps.

Perturbed angular correlation spectroscopy measures the electric field gradient (EFG) at a probe atom site. This can be used to ascertain the local environment of the
probe atom [11]. When probe atoms jump among lattice sites that have EFGs that differ in orientation or magnitude, PAC may be applied to determine the atomic jump frequency by measuring the degree of nuclear relaxation. This method was first applied to study diffusion in solids by Zacate, Favrot and Collins [12, 13]. PAC also has been used to study site preference of impurity atoms in response to change in temperature and/or composition, as in Refs. [6, 7].

Density functional theory (DFT) is a computational method used to calculate electronic properties of solids based on a determination of the electron density of the solid [14-16]. DFT can be used to calculate many properties of solids including formation energies of point defects and, in particular in the implementation in the program WIEN2k, electric field gradients.

PAC experiments were carried out in: the Al$_3$Ni phase, the Al$_3$Ti and the Al$_3$Zr phases [8], and the In$_3$R [17] and the Sn$_3$R phases [18]. The aim of this project was to use DFT to calculate defect properties and site preference effects that will complement PAC studies in this lab. Calculations were performed within density functional theory as implemented in the WIEN2k program [19].
Chapter 2: PAC method

2.1 Introduction

Perturbed angular correlation (PAC) spectroscopy is based on the hyperfine interactions of the nuclear magnetic dipole moment or electric quadruple moment with internal magnetic fields or electric field gradients. These electromagnetic fields exert torques on the moments which result in precession of spins of the probe nuclei. The hyperfine interaction is directly related to the atomic structure of materials, and any change in nuclear environment can cause a change of the electromagnetic field and hence, the hyperfine interaction. Therefore, the PAC technique can be used to investigate material properties on an atomic scale. Details of the PAC technique can be found in references [20-23], and in particular, in reference [21].

The PAC technique employed in this work makes use of radioactive probes that decay through $\gamma - \gamma$ cascades. The directional correlation of the two emitted $\gamma$-rays provides direct information on the electric and magnetic fields at the local environment of the probe.

The work presented in this dissertation involves non-magnetic solids, concerning only electric quadrupole interactions. Therefore, this work will be restricted to electric quadrupole interactions, and also to polycrystalline materials.
2.2 Unperturbed Angular Correlation

The probability of $\gamma$-ray emission from a radioactive nucleus in a particular direction depends on the angle between the angular momentum vector and the direction of emission. Normally spins of radioactive nuclei are randomly oriented in space and the emission pattern of the emitted $\gamma$-rays is isotropic. If the radiation is emitted from a nuclear state which has a preferred spin orientation, the emission pattern can be anisotropic.

Magnetic sublevels are characterized by the quantum number $M$. The selection of nuclei with spin orientation in a particular direction can be attained by detecting one of the two $\gamma$-rays in a cascade. The first gamma-ray $\gamma_1$ is associated with the transition from the initial nuclear state $I_iM_i$ to the intermediate state $IM$ which then decays to the final state $I_fM_f$ following the emission of the second gamma-ray $\gamma_2$. If the populating $\gamma_1$ is detected in a certain direction, nuclei with particular spin orientations of the intermediate state are selected. The distribution pattern of the depopulating $\gamma_2$ is anisotropic because of angular momentum conservation. The anisotropic radiation pattern of $\gamma_2$ is detected with respect to $\gamma_1$ and is called the angular correlation. With no electromagnetic fields present, the population of the $M$-substates does not change, and the resulting radiation pattern is time-independent. This is called unperturbed $\gamma$-$\gamma$ angular correlation.

For two gamma-rays emitted along the directions of $\vec{k}_1$ and $\vec{k}_2$ in an arbitrary coordinate system, the directions of the two emitted $\gamma$-rays can be characterized by spherical polar coordinates $\theta_1, \varphi_1$ and $\theta_2, \varphi_2$ and the angle $\theta$ between $\gamma$-rays. The probability that transitions from the initial state $I_i$ to the intermediate state $I$ and then to
the final state \( I_f \) will emit two radiations \( \gamma_1 \) and \( \gamma_2 \) in directions \( \vec{k}_1 \) and \( \vec{k}_2 \) into detectors one and two, respectively, depends on the angular correlation function, expressed as

\[
W(\vec{k}_1, \vec{k}_2) = W(\theta) = \sum_{0}^{k_{\text{max}}} A_{kk} P_k(\cos \theta).
\]  

(2.1)

The values of \( k \) range from \( 0 \leq k \leq \) minimum of \( (2I, L_1, L_2, L_1', L_2') \) with \( I \) being the spin of the intermediate state and \( L_{1,2} \) and \( L'_{1,2} \) being the multipolarities of the two transitions. The angular correlation coefficients \( A_{kk} \) describe the deviation of the coincidence probability from the isotropic case \( W(\theta) = 1 \) and depend exclusively on nuclear properties. The Legendre polynomials \( P_k(\cos \theta) \) reflect the angular distribution of the two \( \gamma \)-rays. For \( k = 0 \), both the angular correlation coefficient and the Legendre polynomial are equal to unity so that the angular correlation Eq. 2.1 becomes

\[
W(\theta) = 1 + \sum_{k=2}^{k_{\text{max}}} A_{kk} P_k(\cos \theta).
\]  

(2.2)

### 2.3 Perturbed Angular Correlation

A magnetic field or electric field gradient (EFG) at the site of the decaying nucleus interacts with the magnetic dipole or electric quadrupole moment of the probe nucleus, respectively. These hyperfine interactions reduce the degeneracy of the intermediate states corresponding to different quantum numbers \( M \). The extent of energy splitting is related to the strength of the local field. The interaction causes the depopulating \( \gamma \)-ray to be emitted in different directions than it would in the absence of the electromagnetic field. As a result, the angular distribution of the emitted radiation is
time-dependent. This is characterized by a perturbation function $G_{kk}(t)$ which is related to the amount of energy splitting. $G_{kk}(t)$ has the form

$$G_{kk}(t) \sim e^{-i t \Delta E / \hbar} = e^{-i \omega t} \quad (2.3)$$

where $\Delta E = E_m - E_{m'}$ is the energy difference between substates $m$ and $m'$ and the relationship $\omega = \Delta E / \hbar$ is the Larmor theorem. The spin precession frequency $\omega$ enters the angular correlation function (Eq. 2.2) via the perturbation function $G_{kk}(t)$. As a result, the intrinsic angular correlation given by Eq. 2.2 becomes perturbed. For a random polycrystalline sample, in which electromagnetic fields at the sites of probe atoms have random orientations, the angular correlation can be written as

$$W(\theta, t) = \sum_{k_{\text{even}}}^{k_{\text{max}}} A_{kk} G_{kk}(t) P_k(\cos \theta). \quad (2.4)$$

In the presence of an electric field gradient, the perturbation is caused by the interaction of the EFG with the electric quadrupole moment $Q$ of the probe nucleus. This interaction causes spin precessions about the principal axes of the EFG tensor. By selecting an appropriate coordinate system, the EFG tensor can be characterized by three components $V_{xx}$, $V_{yy}$ and $V_{zz}$ along the principal axes and with $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. The EFG tensor is traceless, so that it can be fully described by two parameters, $V_{zz}$ and the EFG asymmetry parameter $\eta$. Here $V_{zz}$ is the largest component of the EFG and the asymmetry parameter is given by

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (0 \leq \eta \leq 1). \quad (2.5)$$
The *asymmetry parameter* $\eta$ is a measure of the deviation of the EFG from the axially symmetric case and is zero if the EFG is axially symmetric ($V_{xx} = V_{yy}$).

The Hamiltonian operator $\hat{H}$ of a nuclear spin with an electric quadrupole interaction is given by

$$
\hat{H} = \frac{eQ_{zz}}{4I(2I-1)} \left[ 3I_z^2 - I(I + 1) + \frac{\eta}{2} (I_+^2 + I_-^2) \right],
$$

where $I_z$, $I_+$, and $I_-$ are the angular momentum operators. For an axially symmetric EFG ($\eta = 0$) the energy difference between two substates is

$$
\Delta E = E_m - E_{m'} = \frac{3eQ_{zz}}{4I(2I-1)} \left| m^2 - m'^2 \right| = 3 \left| m^2 - m'^2 \right| \hbar \omega_Q,
$$

where $\omega_Q$ is defined as:

$$
\omega_Q \equiv \frac{eQ_{zz}}{4I(2I-1)\hbar}.
$$

Since the energy splitting $\Delta E$ is not equidistant between the substates, more than one transition frequency may be observed. For axial symmetry, the fundamental observable quadrupole interaction frequency is given by:

$$
\omega_0 = 3 \omega_Q = \frac{3eQ_{zz}}{4I(2I-1)\hbar} \quad \text{for integer spin,}
$$

$$
\omega_0 = 6 \omega_Q = \frac{6eQ_{zz}}{4I(2I-1)\hbar} \quad \text{for half-integer spin.}
$$
The strength of the electric quadrupole interaction is characterized by the product of the electric quadrupole moment $Q$ and the electric field gradient $V_{zz}$. This quantity, known as the quadrupole coupling constant, is given by

$$
\nu_Q = \frac{eQV_{zz}}{\hbar}.
$$

(2.11)

The experimental perturbation function can be written in the form

$$
G_{kk}(t) = \sum_{n=0}^{n_{\text{max}}} s_{kn} \cos(\omega_n t).
$$

(2.12)

The summation index $n$ in Eq. 2.12 assumes all positive values of $(m^2 - m'^2)$ for integer spins and values $2(m^2 - m'^2)$ for half-integer spins. The parameters $s_{kn}$ are amplitudes of the transition frequencies $\omega_n$. For random polycrystalline samples, the perturbation functions and their amplitudes are independent of sample orientation due to averaging over all possible orientations.

Figure 2.1 shows the hyperfine splittings for $I = 5/2$. For $k_{\text{max}} = 2$ and $I = 5/2$ the angular correlation function reduces to the following form

$$
W(\theta, t) = 1 + A_{22} G_{22}(t) P_2(\cos \theta)
$$

(2.13)

with the perturbation function

$$
G_{22}(t) = s_{20} + \sum_{n=1}^{2} s_{2n} \cos(\eta_0 t), \text{ for } \eta = 0.
$$

(2.14)
Figure 2.1: Electric quadrupole splitting for spin $I = 5/2$ due to an axially symmetric electric field gradient.

For this case the EFGs are characterized by three transition frequencies with $\omega_1 = \omega_0$, $\omega_2 = 2\omega_0$, $\omega_3 = 3\omega_0$ and $\omega_3 = \omega_1 + \omega_2$. The amplitudes of the transition frequencies $s_{2n}$ are mainly determined by the spin $I$ of the intermediate state and are normalized to sum to unity. For axial symmetric, random polycrystalline EFGs and $I = 5/2$, the parameters $s_{2n}$ are $s_{20} = 1/5$, $s_{21} = 13/35$, $s_{22} = 10/35$ and $s_{23} = 5/35$. In the case of the EFG without axial symmetry ($\eta > 0$), the Hamiltonian operator in Eq. 2.6 needs to be diagonalized for each $\eta$ due to the angular momentum operators $I_z, I_+ \text{ and } I_-$. As a result both the transition frequencies $\omega_n$ and their amplitudes $s_{kn}$ change with asymmetry parameter $\eta$. The transition frequencies, for spin $I = 5/2$, have the form [24]

$$\omega_1 = 2\sqrt{3}\alpha \omega Q \sin \left( \frac{\phi}{3} \right), \quad (2.15)$$

$$\omega_2 = 2\sqrt{3}\alpha \omega Q \sin \left( \frac{\pi}{3} \phi \right), \quad (2.16)$$
\[ \omega_3 = 2\sqrt{3}\alpha\omega_q \sin\left(\frac{\phi + \pi}{3}\right). \]  

(2.17)

The coefficients \( \alpha \) and \( \phi \) are given in terms of \( \eta \) by

\[ \phi = \arccos \beta, \]  

(2.18)

\[ \alpha = \sqrt{84(1 + \eta^2)}, \quad \beta = \frac{8\eta}{\alpha^2}(1 - \eta^2). \]  

(2.19)

The factor in parentheses in Eq. 2.19 was found to be \((1 - \eta^2)\) by Collins et al. [23] instead of the factor \((1 - \eta^2/3)\) quoted in Ref. [24]. The perturbation function \( G_{kk}(t) \) is not in general periodic, with the particular exceptions of \( \eta = 0 \) and \( \eta = 1 \), as the individual transition frequencies are not integral multiples of the smallest observable frequency \( \omega_1 \).

However, the relation \( \omega_3 = \omega_1 + \omega_2 \) is still valid as can be seen from Fig. 2.1. For this case, \( G_{kk}(t) \) has the form

\[ G_{kk}(\eta, t) = \sum_{n=0}^{n_{\text{max}}} s_{kn}(\eta)\cos[n\omega(\eta)t] \]  

(2.20)

and the angular correlation is

\[ W(\theta, t) = \sum_{k=\text{even}}^{k_{\text{max}}} A_k \gamma_k G_{kk}(\eta, t) P_k(\cos \theta). \]  

(2.21)

where \( \gamma \) is an angular attenuation factor. For random polycrystals the amplitudes \( s_{kn}(\eta) \) are roughly equal to \( s_{kn}(0) \). The ratio \( \omega_1/\omega_2 \) obtained experimentally from fits of the experimental angular correlation spectrum can be used to determine the asymmetry parameter.
Often probes are located in more than one lattice location in a sample, which leads to multiple perturbations. The resulting perturbation function $G_{22}^{\text{total}}$ is given by the superposition of the individual perturbation functions,

$$G_{22}^{\text{total}}(t) = \sum_i f_i G_{22,i}(t), \quad (2.22)$$

where $f_i$ is the amplitude of the $i^{th}$ perturbation function such that:

$$\sum_i f_i = 1 \quad (2.23)$$

And $G_{22,i}$ written as:

$$G_{22,i} = \sum_{n=0}^{3} s_{2n,i}(\eta_i) \cos(\omega_{n,i} t). \quad (2.24)$$

A small distribution of EFGs at one site of the probes results in a distribution of transition frequencies. Such variations could be caused, for example, by distant point defects or lattice imperfections that produce weak EFGs. The distributions were characterized by fitting with a perturbation function

$$G_{22,i}(t) = \sum_{n=0}^{3} s_{2n,i}(\eta_i) \cos(\omega_{n,i} t) \exp \left[ -\frac{(\frac{\omega_{n,i} t}{\sigma_i})^p}{p} \right]. \quad (2.25)$$

Here the parameter $\sigma_i$ is the width of the frequency distribution, and $p = 1$ for a Lorentzian distribution and $p = 2$ for a Gaussian distribution.
2.4 PAC Probe Atoms

Choosing a suitable radioisotope probe for PAC study depends on many factors. A PAC measurement requires the detection of two different \( \gamma \)-rays. Thus, ideally the two \( \gamma \)-rays should have resolvable energies. The lifetime of the parent atom should be of the order of several days so that sufficient time is available for sample preparation and measurements. The lifetime \( \tau \) of the intermediate state or PAC level determines the time window in which the spin precession frequency can be observed. The time resolution of the detector (less than \( \sim 1 \) ns for \( \text{BaF}_2 \) crystals) sets the lower limit of \( \tau \). The upper limit is set by signal-to-noise ratio considerations. A source activity of the order of \( 10^5 \) - \( 10^6 \) Bq is practical and \( \tau \) of the PAC level should be approximately 10 ns to several microseconds. A large value (> 0.1 b) of the electric quadrupole moment is advantageous for detecting weak EFGs. Large values of \( A_{kk} \) are useful as they determine the amplitude of modulation and enable the observation of the perturbations effectively.

Commonly used PAC probes are \(^{100}\text{Pd}/\text{Rh}, \) \(^{111}\text{In}/\text{Cd} \) and \(^{181}\text{Hf}/\text{Ta}. \) However, \(^{111}\text{In}/\text{Cd} \) is used most often and was used exclusively for experiments in this work. Figure 2.2 shows the decay scheme of \(^{111}\text{In}/\text{Cd}. \) To obtain the measured EFG value from observed QI frequencies, the quadrupole moment \( Q(5/1^+) = +0.83(13) \) b [21] was used.
Figure 2.2: Decay scheme of $^{111}$In/Cd (from Ref. [21]).

2.5 Experimental Setup and Data Recording

Measurements were carried out using a four-detector fast-slow PAC spectrometer with BaF$_2$ scintillator detectors located at 90º angles in a plane, as shown in Fig. 2.3. Model numbers of PAC electronics are listed in the Appendix. The timing signals are taken from the fast anode outputs (F) of the photomultiplier tubes (PMT) and are shaped using constant-fraction differential discriminators (CFDD). Energies of the $\gamma$-rays are taken from the slow dynode outputs (S) of the PMTs and are discriminated using single-channel analyzers (SCA) after amplification by amplifiers (AMP). Timing signals from detectors 1 and 2 are used to start the time-to-amplitude converter (TAC), while signals from detectors 3 and 4 stop the TAC. Signals from the “stop” detectors are delayed using a digital delay generator (DDG). By delaying time-zero to the middle of the time spectrum and using single-channel analyzers to check energy signals for gamma ray
energies of $\gamma_1$ and $\gamma_2$, one obtains double-sided spectra at relative angles of 90° and 180°, as shown in Fig. 2.4.

Figure 2.3: PAC electronics schematic.
The perturbation function $G_{22}(t)$ is extracted algebraically from four coincidence spectra for detector pairs $i$ and $j$, two at relative angles of $180^\circ$ (pairs $1-3$ and $2-4$) and two at relative angles of $90^\circ$ (pairs $1-4$ and $2-3$):

$$C_{ij}(\theta,t) = N_{ij}(W(\theta,t) + B_{ij}), \quad \text{(2.26)}$$

in which $N_{ij}$ is the number of true coincidences and $B_{ij}$ is the accidental background. After preliminary computer fitting and subtraction of backgrounds, pairs of coincidence spectra at each angle are geometrically averaged to form coincidence spectra at $90^\circ$ and $180^\circ$: $C(\pi,t)$ and $C(\pi/2,t)$. It can be shown that the experimental perturbation function $G_{22}(t)$ is then given by the ratio function:

$$G_{22}(t) = \frac{2}{A_{22}r_a} \frac{C(\pi,t) - C(\pi/2,t)}{C(\pi,t) + 2C(\pi/2,t)}. \quad \text{(2.27)}$$

The solid-angle attenuation factor $r_a$ can be estimated from the experimental geometry to a precision of several percent, which is adequate for present purposes. The transition frequencies $\omega_n$ can be found by fitting the experimental ratio function with the theoretical perturbation function (Eq. 2.14). In practice, $G_{22}(0) \neq 1$ due to uncertainty in angular
attenuation factor \( \gamma \) and/or effects of high counting rates. Therefore, all measurements are normalized to \( G_{22}(0) = 1 \).

2.6 Sample Preparation

PAC sources were made using carrier-free \(^{111}\)In activity in 0.05 molar HCl solution purchased from Perkin/Elmer. Samples were prepared by drying a drop of activity on high purity metal foils and then arc-melting the foils under high purity Argon gas. Typical sample masses were between about 50 and 100 mg. Samples were weighed before and after arc melting to determine weight loss due to vaporization. Weight loss leads to uncertainty in sample composition. The concentration of In-probes in the samples was very dilute, around 0.1 ppb, ensuring that the probes had negligible effect on the samples. Samples were annealed after arc melting to promote good crystal ordering and grain growth.

2.7 Equilibrium measurements at high temperature

PAC spectra that were collected at high temperatures up to 1200K were done so under \( 10^8 \) mBar vacuum inside the PAC oven surrounded by four scintillation detectors as shown in Fig. 2.5. Samples were heated in a cylindrical molybdenum crucible by three tungsten filaments (shown in red in Fig. 2.5) that were located about 1 cm from the sample and extending from an upper ring to a lower ring. The crucible was supported by an \( \text{Al}_2\text{O}_3 \) thermocouple tube connected to a vacuum flange port via three stainless steel
support wires. Temperature measurement and control was provided by a K-type thermocouple that passes through the bottom of the crucible so that the sample rests on the thermocouple junction. Two cylindrical molybdenum heat-baffles (not shown) were placed around the heating assembly.

It was found that measurements made at high temperature under high vacuum could lead to significant indium evaporation from rare-earth indide samples. Consequently, the composition of the sample would change over time. In order to reduce evaporation, samples tending to lose In were wrapped in 0.001 inch thick iron foil. This reduced In evaporation because indium is insoluble in iron and indium and iron liquids are immiscible. PAC spectra were collected for ~24 hours per measurement for most samples and for ~8 hours per measurement for samples that had significant In evaporation.
Figure 2.5: PAC oven surrounded by four scintillation detectors (left) and heating assembly (right) inside the oven.
Chapter 3: Density functional theory

3.1 Introduction

To calculate quantitative properties of solids, the time-independent Schrödinger equation is solved:

$$\hat{H}\Psi = E\Psi. \quad (3.1)$$

where $\Psi$ is the wave function of the crystal, $E$ the energy eigenvalues and $\hat{H}$ the Hamilton operator.

The solid is described as a system of interacting charged particles consisting of nuclei of positively charged ions at positions $\vec{R}_a$ and much lighter electrons at positions $\vec{r}_i$. For $N$ atoms with atomic number $Z$, the problem is to solve a many-body system of $N+ZN$ electromagnetically interacting bodies, for which the exact non-relativistic Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2} \sum_a \frac{\psi_{\vec{r}_a}^2}{M_a} - \frac{\hbar^2}{2} \sum_i \frac{\psi_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\varepsilon_0} \sum_{a,i} \frac{e^2 Z_a}{|\vec{R}_a - \vec{r}_i|}$$

$$\quad + \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\varepsilon_0} \sum_{a \neq b} \frac{e^2 Z_a Z_b}{|\vec{R}_a - \vec{R}_b|} \quad (3.2)$$

with $M_a$ being the mass and $Z_a$ the charge of nucleus $a$ at position $\vec{R}_a$, and $m_e$ the electron mass at position $\vec{r}_i$. The terms in Eq. 3.2 describe, in order: the kinetic energy operator for nuclei $a$ of the system, the kinetic energy operator of electrons $i$, the Coulomb interaction between electrons $i$ and nuclei $a$, the Coulomb interaction between...
electrons $i$ with other electrons $j$, and finally the last term is the Coulomb interaction between nuclei $a$ and $b$. The Schrödinger equation can be solved exactly only for one-electron systems. For solids that contain Avogadro’s number of atoms, approximations are required.

3.2 Born-Oppenheimer Approximation

Nuclei are much heavier and thus much slower than electrons, so they are assumed to be "frozen" at fixed positions, and the electrons will instantaneously equilibrate with them. Since the nuclei do not move, their kinetic energy is zero, the first term in Eq. 3.2 disappears, and the last term becomes a constant. This is known as the \textit{Born-Oppenheimer approximation} \cite{25}. Within this approximation, the Hamiltonian can be written as

\[ \hat{H} = \hat{T} + \hat{V} + \hat{V}_{\text{ext}}, \]  

(3.3)

where $\hat{T}$ is the kinetic energy of the electrons, $\hat{V}$ is the potential due to the electron-electron interaction, and $\hat{V}_{\text{ext}}$ is the potential energy of electrons in the external potential caused by the fixed nuclei.

3.3 Hohenberg and Kohn

Hohenberg and Kohn \cite{14} worked on the problem of electrons in a periodic potential. They proved that every observable of a stationary quantum mechanical system
is determined by the ground state density $\rho$ alone $\langle \Psi | \hat{O} | \Psi \rangle = O[\rho]$. Taking $\hat{O}$ to be the Hamiltonian $\hat{H}$, the ground state total energy functional $H[\rho] = E_{\text{tot}}[\rho]$ is of the form

$$E_{\text{tot}}[\rho] = \int V_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r} + F_{\text{HK}}[\rho].$$

(3.4)

where $F_{\text{HK}}[\rho]$ is the Hohenberg-Kohn density functional. The exact ground state density of a system in a particular external potential $V_{\text{ext}}(\vec{r})$ is the density that minimizes $E_{\text{tot}}[\rho]$. The charge density $\rho$ is the main variable in DFT. The functional $F_{\text{HK}}[\rho]$ is independent of the external potential $V_{\text{ext}}(\vec{r})$ and is applicable to any arbitrary system. However, the form of the functional $F_{\text{HK}}[\rho]$ is unknown \textit{a priori}.

The Hohenberg-Kohn functional can be divided into three terms:

$$F_{\text{HK}}[\rho] = T_0[\rho] + V_H[\rho] + V_{\text{xc}}[\rho],$$

(3.5)

where $T_0[\rho]$ is the kinetic energy of a non-interacting electron gas, $V_H[\rho]$ is the Hartree potential due to the electron density distribution and the ionic lattice and $V_{\text{xc}}[\rho]$ is the exchange-correlation potential which accounts for self-interactions within the electron gas.

### 3.4 Kohn-Sham equations

Kohn and Sham [15] developed a way to obtain the ground state density. The exact ground state electron density of an $N$-electron system is

$$\rho(\vec{r}) = \sum_{i=1}^{N} \phi_i^*(\vec{r}) \phi_i(\vec{r}),$$

(3.6)
where the single-particle wave functions $\phi_i(\vec{r})$ are the lowest energy solutions of the Kohn-Sham equation

$$\hat{H}_{KS}\phi = E\phi,$$  \hspace{1cm} (3.7)

with $\hat{H}_{KS}$ given by

$$\hat{H}_{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r})}{|\vec{r}' - \vec{r}|} d^3\vec{r}' + \hat{V}_{ext} + \hat{V}_{xc}.$$  \hspace{1cm} (3.8)

The first term in Eq. 3.8 is the functional for the kinetic energy $\hat{T}_0$ of a non-interacting electron gas, the second term is the Hartree potential $\hat{V}_H$, $\hat{V}_{ext}$ is the external potential arising from the fixed nuclei, acting on the electrons and $\hat{V}_{xc}$ is the exchange correlation potential which accounts for self-interactions. The exchange-correlation potential is given by the functional derivative

$$\hat{V}_{xc} = \frac{\partial v_{xc}[\rho]}{\partial \rho}.$$  \hspace{1cm} (3.9)

The exchange correlation potential is only dependent on the electron density $\rho$ at position $\vec{r}$ and thus is a local potential. The Hartree potential and the exchange-correlation potential depend on the electron density, which in turn depends on them through the Kohn-Sham equation. As such, the Kohn-Sham equation constitutes a self-consistent problem which is solved by an iterative process. An initial guess of the $\rho_0(r)$ is used to construct the corresponding potentials. Then, the Kohn-Sham equation is solved and a new electron density $\rho_n(r)$ is constructed from the solution. This process is repeated until
the prescribed convergence criteria are met. In WIEN2k, this process is called the self-consistent field (SCF) cycle.

3.5 The Exchange-Correlation Functional

Within the Born-Oppenheimer approximation, the Kohn-Sham scheme is exact. However, an approximation to the yet unknown exchange-correlation functional still must be made. Two common approximations are called the local density approximation (LDA) and the generalized gradient approximation (GGA).

In the local density approximation the exchange-correlation functional is approximated by

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{xc}^{LDA}[\rho(\vec{r})] d\vec{r},$$

(3.10)

where $\varepsilon_{xc}^{LDA}$ is the exchange-correlation density of a homogeneous electron gas, which only depends on the electron density $\rho(\vec{r})$. This exchange-correlation functional can be split into two components:

$$E_{xc}^{LDA} = E_{x}^{LDA} + E_{c}^{LDA}.$$  

(3.11)

The first contribution $E_{x}^{LDA}$ is the exchange energy that comes from the Pauli exclusion principle. In the LDA it is assumed that at any position $\vec{r}$ the exchange energy of the real system (inhomogeneous electron gas) can be approximated by the corresponding energy of the homogeneous electron gas of the same density. For the latter the exact formulation is known and scales approximately as $E_x \propto \rho^{4/3}$. The second contribution, called the
correlation energy $E^{\text{LDA}}_c$, originates from the interaction of electrons having the same spin. Both terms $E_x$ and $E_c$ can be calculated using quantum Monte-Carlo methods [26].

While LDA uses the exchange energy density of the uniform electron gas, disregarding inhomogeneity of the real charge density, the generalized gradient approximation (GGA) includes such inhomogeneity by including the gradient of the electron density in the functional:

$$E^{\text{GGA}}_{xc} = \int \rho(\vec{r}) \epsilon^{\text{GGA}}_{xc} [\rho(\vec{r}), \nabla \rho(\vec{r})] d\vec{r}. \quad (3.12)$$

For practical calculations a parameterized form of the functional $\epsilon^{\text{GGA}}_{xc}$ must be implemented. The parameterization used for the calculations in this work is that of Perdew, Burke and Ernzerhof (PBE) [27].

3.6 The (L)APW+lo Method

To solve the Kohn-Sham [15] equation (3.7) a number of different methods have been developed. From the Bloch Theorem, boundary conditions for the single particle wave function can be derived. A general solution for these wave functions can be obtained with plane waves. Plane waves constitute a complete and orthogonal basis set. However, strong fluctuations appear in the wave function close to a nucleus. To describe these fluctuations a large number of plane waves would be required. To reduce the number of plane waves, Slater [28] proposed to augment the plane wave basis set in the region close to the nucleus with basis functions that are more suitable for the description
of atomic wave functions. This resulted in the \textit{Augmented Plane Wave} (APW) method \cite{28}. In the APW method the unit cell is divided into two regions: (I) non-overlapping “muffin-tin” (MT) spheres with radius $R_{MT}$ centered at each atom and (II) the interstitial region. Within $R_{MT}$ wave functions are represented as linear combinations of radial functions $u_i(r, E_i)$ multiplied by angular dependent spherical harmonics $Y_{lm}(\hat{r})$:

$$
\phi_{k_n}^{APW} = \sum_{l,m} A_{lm,k_n} u_i(r, E_i) Y_{lm}(\hat{r}), \quad r \in MT.
$$

Within the interstitial region the wave functions are expanded in plane waves:

$$
\phi_{k_n} = \frac{1}{\sqrt{V}} e^{i\vec{k}_n \vec{r}}, \quad r \in I,
$$

where $\vec{k}_n = \vec{k} + \vec{K}_n$ with $\vec{k}_n$ as the wave vector of the \textit{first Brillouin zone}, $\vec{K}_n$ is the reciprocal lattice vector, and $V$ is the volume of the unit cell. The coefficients $A_{lm}$ are functions of $k_n$ and are calculated under the condition that the wave functions are continuous in value (not in slope) at the sphere boundary. However, this particular basis set leads to a non-linear eigenvalue problem, which is difficult to solve.

It was proposed by Andersen \cite{29} to expand the energy dependence of radial wave functions inside the muffin-tin spheres with its energy derivative and thus established the \textit{Linearized Augmented Plane Wave} (LAPW) method.

In the LAPW method the radial functions are linearized and the problem is reduced to a linear eigenvalue problem. This is accomplished by performing a Taylor expansion of the radial function in $E_i$ around $E_{i,1}$ to first order:
The linearization energy $E_{1,l}$ is chosen such that it is close to the expected eigenvalue. Wave functions within the muffin-tin become

$$\phi^{\text{LAPW}}_{k_n} = \sum_{l,m} [A_{lm,k_n} u_l(r, E_{1,l}) + B_{lm,k_n} \dot{u}_l(r, E_{1,l})] Y_{lm}(\hat{r}), \quad r \in MT. \quad (3.16)$$

The coefficients $A_{lm,k_n}$ and $B_{lm,k_n}$ are calculated under the conditions that wave functions are continuous both in value and slope at the sphere boundary and are normalized. In the interstitial region, the basis set is the same as in the APW method, but in the muffin-tin spheres, the basis functions not only depend on $u_l$, but also on its energy derivative $\dot{u}_l$. As such, the LAPW method is more flexible than the APW in the muffin-tin spheres.

Electrons can be divided into two types based on whether or not they participate in chemical bonding. Electrons that are closely bound to their nucleus and are entirely localized in the muffin-tin sphere are called core electrons. Valence electrons are electrons that “leak” out of the muffin-tin sphere and bond with other atoms. However, some electrons cannot be clearly distinguished. Some states are neither constrained in the core states nor lie in the valence state and are correspondingly called semi-core states. These states have the same angular quantum number $l$ as the valence states but have lower principal quantum number $n$. Consequently it is difficult to use one $E_i$ to determine wave functions with the two same $l$ in Eq. 3.16. To solve this, local orbitals (LO) are added:
Each local orbital is zero in the interstitial region and in other atoms’ muffin-tin sphere. The coefficients $A_{lm}$, $B_{lm}$ and $C_{lm}$ are determined by requiring the LO to have both zero value and zero slope at the muffin-tin boundary and to be normalized.

Sjöstedt, Nordström and Singh [30] demonstrated that the standard LAPW method is not the most efficient way to linearize Slater's APW method and therefore introduced the APW+lo method. Like the original APW method, the APW+lo method is energy independent and has the same basis size. To achieve this, a local orbital (lo) is added which is different from the LOs used to describe semi-core states. This new local orbital $lo$ is given by

$$\phi_{lm}^{lo} = \sum_{t,m} \left[A_{tm} u_t(r, E_{1,t}) + B_{tm} \hat{u}_t(r, E_{1,t}) + C_{tm} u_t(r, E_{2,t})\right] Y_{lm}(\hat{r}) \quad r \in MT. \quad (3.17)$$

The APW+lo basis set looks much like the LAPW basis set, but here the coefficients $A_{tm}$ and $B_{tm}$ are not dependent on $k_n$. They are determined by the requirements that the $lo$ is normalized and its value is zero at the sphere boundary. The advantage of the APW+lo method is that it has the same small basis set size as the APW method and has the same accuracy compared to the LAPW method.

It is possible to use a hybrid basis set, LAPW in combination with APW [(L)APW+lo], and treat the physically important orbitals by the APW+lo method, but the polarization $l$-quantum numbers with LAPW. All calculations presented in this work used a hybrid basis set (L)APW+lo. This basis set is used to expand the wave function

$$\phi_{lm}^{lo} = [A_{tm} u_t(r, E_0) + B_{tm} \hat{u}_t(r, E_0)] Y_{lm}(\hat{r}) \quad r \in MT. \quad (3.18)$$
\[ \Psi(r) = \sum_n c_n \phi_{k_n} \]  

(3.19)

For DFT calculations the energy cutoff \( E_{\text{cut}} \) and \( k \)-mesh (\( k \)-points) are important basis set parameters to determine the accuracy of the computational results. Both parameters must be tested in DFT calculations in order to find the optimum compromise between accuracy and implied computational burden. When plane waves are used to construct wave functions, in principle the more plane waves, the better the results are. However, it is not necessary to use infinitely many plane waves to construct the wave function. The number of plane waves used is limited by the energy cutoff parameter \( E_{\text{cut}} \). The relationship between energy cutoff and plane wave coefficient is

\[ E_{\text{cut}} = \frac{\hbar^2 K_{\text{max}}^2}{2m_e}. \]  

(3.20)

The wave function based on \( K_{\text{max}} \) is

\[ \Psi_{k_n}(\vec{r}) = \sum_{K}^{K_{\text{max}}} g_{k_k} e^{-i(k+K)\cdot r}. \]  

(3.21)

In the (L)APW+lo method this energy cutoff is employed in the interstitial region. For the MT sphere, the spherical harmonics should also be terminated at a maximum \( lm \) for the same reason.

### 3.7 Solving the Schrödinger Equation

Using the basis set above, the one-electron Kohn-Sham equations (Eq. 3.7) can be solved using the Rayleigh-Ritz variational principle. The elements of the Hamilton- and
overlap-matrix are calculated, and the resulting generalized eigenvalue problem is solved. For the calculation of the Hamilton-matrix elements a full potential (FP) is used, i.e. there is no approximation in the description of the potential. The potential is represented by a Fourier series in the interstitial region and by radial dependent functions multiplied by lattice harmonics functions inside the atomic spheres. The results of the generalized eigenvalue problem are energy eigenvalues of the crystal wave function from which the variational coefficients of the trial function can be calculated.

### 3.8 Relativistic Effects

Non-relativistic quantum mechanics, described by Schrödinger's wave equation, is successful for solids containing light elements in which the velocity of the electron is small compared with the speed of light. However, for heavier elements relativistic effects cannot be neglected. The relativistic mass increase is particularly important in heavy atom systems as can be seen from Bohr's model that speed scales with atomic number, $Z$. Spin, which is a fundamental property of the electron, is not built into Schrödinger's equation. An appropriate equation for the electron should incorporate relativistic effects and spin. Such a relativistic description of quantum mechanics is found in the Dirac equation:

$$i\hbar \frac{\partial \psi}{\partial t} = \left[ c\alpha \cdot \left( \vec{p} - \frac{a}{c} \vec{A} \right) + \beta mc^2 + qV \right] \psi. \quad (3.22)$$

Where $\vec{p}$ is the momentum operator, $\vec{A}$ is a vector potential, $V$ is a scalar potential, and $\alpha$ and $\beta$ are the 4 x 4 Dirac Matrices,
Here, $\sigma$ are the 2x2 Pauli matrices and $I$ is the 2x2 identity matrix. The wave functions are four-component column vectors written as:

$$
\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix},
$$

where $\phi$ and $\chi$ are two component spinors [31, 32].

The Dirac equation not only takes the relativistic kinetic energy of the electron into account, but spin and fine structure corrections also come out. It follows that spin and spin-orbit effects are relativistic effects. This can be seen explicitly by splitting the Dirac equation into two coupled equations in $\phi$ and $\chi$, setting $\vec{A} = 0$, and assuming $V$ is spherically symmetric. To order $p^4$, one gets the following Hamiltonian

$$
\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(r) - \frac{mc}{8} \left( \frac{\hat{p}}{mc} \right)^4 + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \left( \vec{L} \cdot \vec{S} \right) - \frac{\hbar}{4m^2c^2} \frac{dV}{dr} \frac{\partial}{\partial r}.
$$

The first and second terms contain the non-relativistic Schrödinger equation. The third term is the relativistic correction to the kinetic energy or mass. The fourth term corresponds to spin-orbit coupling, and the last term is the so-called Darwin correction. The Darwin term can be thought of as a relativistic correction to the potential [33].

Some physical consequences of the mass correction term, called the scalar term, are the contraction of $s$- and $p$-electron orbitals in atoms. The $s$- and $p$-electrons have a large probability density near the nucleus and, thus, tend to move at speeds near $c$. In
what is known as the direct relativistic effect, the corresponding mass increase contracts the orbitals. As a consequence, the \( d \)- and \( f \)-orbitals will expand a little due to shielding effects. That is, they undergo indirect relativistic effects [34].

3.9 Electric Field Gradient

Nuclei with nuclear spin quantum number \( I \geq 1 \) have a non-spherical nuclear charge distribution and an electric quadrupole moment \( Q \). The nuclear quadrupole interaction can be used to probe the electronic charge distribution which surrounds the site of such a nucleus. The EFG at the nuclear position is produced mainly by valence electrons inside the atomic sphere. The symmetric and traceless EFG tensor always can be diagonalized and specified completely by two independent real parameters. The main principal component of the EFG, \( V_{zz} \), and the asymmetry parameter \( \eta \) usually are used to characterize the EFG in the principal axes system. These two quantities can be determined from experiment.

The principal component of the EFG tensor is predicted using density functional theory calculations from the formula [35]:

\[
V_{zz} = \lim_{r \to \infty} \sqrt{\frac{5}{4\pi}} \frac{V_{20}}{r^5},
\]

(3.26)

where the radial potential coefficient, \( V_{20} \), is given by

\[
V_{20}(r = 0) = \frac{1}{5} \int_0^{R_{mt}} \frac{d^3 \rho}{r^3} \left[ 1 - \left( \frac{r}{R_{mt}} \right)^5 \right] d^3 r + 4\pi \sum_K V(K) j_2(KR_{mt}) Y_{20}(K).
\]

(3.27)
The integrals yield the EFG contribution of the electrons inside and over the surface of the muffin-tin sphere. The summation yields the EFG contribution of the electrons outside the spheres. The contribution of the electrons inside the sphere has been called the valence EFG. The contributions of the electrons over the surface and outside the spheres has been termed the lattice EFG.

3.10 WIEN2k

Calculations were performed using the WIEN2k computer program [19]. This program is an implementation of the (L)APW+lo method for the calculation of electronic properties of crystals. An extended description can be found in [36, 37]. WIEN2k consists of a number of programs written in FORTRAN that are linked together with csh shell scripts and features a web-based graphical interface called w2web. WIEN2k is split into two parts: the initialization process and the self-consistent filed cycle (SCF).

During the initialization process, WIEN2k generates a number of input files for the different programs. Before a SCF cycle can be started an initial electron density has to be known in order to calculate the potential. During the initialization phase the following programs are run:

- \textit{nn} - calculates nearest-neighbor distances and tests for overlapping muffin-tin spheres.

- \textit{sgroup} - determines the spacegroup as well as all pointgroups of non-equivalent sites.
- *lstart* - solves the Schrödinger (Dirac) equation for the free atoms and calculates their electron densities.

- *symmetry* - generates the symmetry operations for the given atomic position and crystal structure, determines the point group of the atomic positions and generates the corresponding $lm$-combinations for the lattice harmonics.

- *kgen* - generates a $k$-mesh in the irreducible part of the Brillouin zone.

- *dstart* - calculates a starting density by superposition of electron densities.

In the SCF cycle the calculation is repeated until given convergence criteria are met. During the SCF cycle the following programs are executed:

- *lapw0* - calculates the total potential $V_{\text{tot}}$ as the sum of Coulomb $V_C$ (Hartree potential) and exchange correlation potential $V_{\text{xc}}$, which are generated from the input density.

- *lapw1* - calculates Hamilton- and overlap matrix elements. By diagonalizing the general eigenvalue problem the eigenvectors and energy eigenvalues are calculated.

- *lapw2* - calculates the Fermi level and the valence charge density from Kohn-Sham orbitals specified by the eigenvectors.

- *lcore* - calculates the eigenvalues and charge-densities for the core states.

- *mixer* - calculates the total electron density from the core and valence states for the next cycle. The output density is mixed with the old input density using the Pratt [38] or Broyden-II [39] scheme to ensure convergence during the SCF cycle.
Some structures have free internal structural parameters which can either be taken from experiment or optimized using the calculated forces on the nuclei. The program *mini* automatically determines the equilibrium positions of all individual atoms that are not constrained by symmetry. Equilibrium lattice parameters are determined by minimizing the total energy of the cell as a function of cell volume for cubic crystals or by cell volume and $c/\alpha$ ratio for hexagonal and tetragonal crystals.

### 3.11 WIEN2k calculation details

Details of density functional theory calculations for systems studied in this work are provided in the Appendix. Muffin-tin radii for all atoms are listed in Table A1. Tables A2 – A13 tabulate $k$-point and $R_{MTK_{\text{MAX}}}$ convergence tests. For all systems, exchange and correlation effects were treated using GGA (PBE) [27]. Energy separation between the band- (semi-core and valence) and core-states was -6.0 Ry. Inside the muffin-tin spheres, the wave functions, the electron charge densities, and the potentials are expanded in terms of spherical harmonics up to angular momenta $l_{\text{max}}=10$. For $k$-point and $R_{MTK_{\text{MAX}}}$ convergence tests, lattice optimization and site energy calculations, the SCF iteration process ran until the difference in energy between successive iterations was less than $eC = 0.0001$ Ry. For site EFG calculations, the SCF iteration process ran until the difference in energy and integrated charge density between successive iterations was less than $eC = 0.0001$ Ry and $cc = 1.0\ e$ respectively.
To test $k$-points and $R_{MTK_{MAX}}$ convergence, conventional (1x1x1) unit cells constructed with experimental lattice parameters were used. First, the total energy of the cell was calculated as a function of $k$-points with $R_{MTK_{MAX}}$ fixed at 7.0. The number of $k$-points was chosen such that the difference in energy between successive runs was less than 0.001 eV. Next, keeping the number of $k$-points fixed, the total energy of the cell was calculated as a function of $R_{MTK_{MAX}}$. The value of $R_{MTK_{MAX}}$ was chosen such that the difference in energy between successive runs was less than 0.01 eV. Plots of energy versus $k$-points and $R_{MTK_{MAX}}$ are shown below in Figs. A1 - A5 for Al$_3$Ni, Al$_3$Ti, Al$_3$Zr, In$_3$La and In$_3$Lu. Results of convergence test for bulk metals are shown in Table A2. Values obtained from convergence tests were used to optimize lattice parameters. The number of $k$-points used in 2x2x1-Al$_3$Ti, 2x1x1-Al$_3$Zr, 2x2x2-In$_3$La and 2x2x2-In$_3$Lu supercell calculations was chosen such that the energy difference between the corresponding 1x1x1 unit cell and the supercell was less than 0.01 eV. The value of $R_{MTK_{MAX}}$ used in supercell calculations was equal to the conventional unit cell $R_{MTK_{MAX}}$ value.

Structural parameters including lattice volumes, $c/a$ and $b/a$ ratios where appropriate, and internal atomic positions when not determined by symmetry were determined by energy optimization. As an initial step, optimized lattice parameters were obtained for Al$_3$Ti, Al$_3$Zr, In$_3$La, and In$_3$Lu by calculating ground state energies of conventional unit cells for different volumes and then fitting energy as a function of volume to a fourth order polynomial; the local minimum of the polynomial then corresponds to the optimized lattice volume. Additionally, for tetragonal Al$_3$Ti and
Al$_3$Zr structures, optimized $c/a$ ratios were found by fitting energy as a function of $c/a$ ratio to a fourth order polynomial. For orthorhombic Al$_3$Ni, 3D optimization was achieved by calculating the ground state energies for different values of $b/a$, $c/a$ and volume and selecting the combination that had the lowest energy. Unit cell volumes of all structures were optimized with atoms occupying their ideal lattice positions. In addition, after lattice optimization, atoms having free internal structural parameters in Al$_3$Ni and Al$_3$Zr were allowed to relax from their ideal lattice sites to their equilibrium positions until forces acting on the nuclei were less than 1.0mRy/bohr. Listed in Table A3 are measured and DFT optimized lattice parameters for Al, In, La, Lu, Ni, Ti and Zr bulk metals.
Chapter 4: Al₃Ni

4.1 Introduction

The preference of indium solutes for different lattice sites in the intermetallic Al₃Ni having the orthorhombic $DO_{20}$ structure was studied using PAC. The orthorhombic $DO_{20}$ structure has two inequivalent Al-sites and one Ni-site. Site preference was determined as a function of composition through measurements of nuclear quadrupole interactions using PAC. Observed QI signals were correlated with crystal sites, and site fractions observed at room temperature to determine the site preference. Measurements were made on samples having compositions of 23.0, 25.5, 27.5, and 33.0 at.% Ni. For Ni-rich samples, indium was observed to occupy one of the two Al-sites, as observed by a prominent quadrupole interaction at room temperature with fundamental frequency $\omega_1 = 263.0(1)$ Mrad/s and electric field gradient asymmetry parameter $\eta = 0.78(2)$. For the Ni-poor sample, the spectrum largely exhibited an ill-defined quadrupole interaction that was attributed to indium being located in grain boundaries or similar irregular sites that have a great multiplicity of local atomic configurations and, consequently, electric field gradients.

A previous study was made of site preferences of In solutes in five phases (Ni$_2$Ga, Pt$_2$Ga, Ni$_2$Al$_3$, Pd$_2$Al$_3$, and Pt$_2$Al$_3$) having the $D5_{19}$ structure [6]. For Ni$_2$Al$_3$, measurements were made at room temperature on samples having seven compositions. Occupied sites were identified by comparison with quadrupole interactions of probes in three indides having the same structure, Ni$_2$In$_3$, Pd$_2$In$_3$ and Pt$_2$In$_3$, and by comparison of
site EFGs calculated using a simple point-charge approximation. For Ni-rich compositions, indium solutes were found to occupy predominantly one of the two inequivalent Al-sites. For Ni-poor Ni$_2$Al$_3$ alloys, the predominant signal instead was highly inhomogeneous. This was attributed to indium solutes on non-crystallographic sites such as in grain boundaries. The same behavior was observed for Pt$_2$Al$_3$ and Pd$_2$Al$_3$, but not for the two gallides Ni$_2$Ga$_3$ and Pt$_2$Ga$_3$. In the Ga-rich gallides, indium impurities were observed to occupy well-defined sites with very low QI frequencies that were attributed to indium on $TM$-sites ($TM = \text{transition metal}$), where they would be surrounded by eight Ga-atoms in a slightly distorted cube.

Earlier measurements on Al-Ni alloys included studies of point defects in NiAl [40, 41] and detection of boundary compositions of the neighboring Ni$_2$Al$_3$ and NiAl phases through observations of QI signals characteristic for each phase [42]. Solutes in off-stoichiometric phases generally were observed to locate on the sublattice of and element in which there is a deficiency, thereby reducing the overall defect count. Additionally, no In solutes were observed to occupy lattice sites that are completely surrounded by Al-atoms.

The difference in site preference in Al$_3$Ni can be understood in terms of relative energies needed to locate an indium solute in the Al-site, the Ni-site and grain-boundary sites. In Ni-rich alloys, the energy is minimized when indium solutes occupy empty Al-sites, in accord with the general rule that solutes tend to locate on sublattices in which there is a deficiency. In Al-rich alloys, indium was not observed to populate the empty
Ni-sites. The energy to fill an Al-site is apparently large due to additional energy needed to displace an Al-atom in Al-rich alloys. This is attributed to the fact that the Ni-site is completely surrounded by Al-atoms, and indium is essentially insoluble in Al metal [43].

To complement the Al$_3$Ni PAC study, DFT calculations were performed to determine site enthalpies for In-impurities and site EFGs for Cd-impurities in Al$_3$Ni. The parent of the radioisotope PAC probe, $^{111}$In, has a mean life of 4.0 days. This is sufficient time for probes to equilibrate to sites of lowest energy in Al$_3$Ni. Site enthalpies were calculated for In-impurities in Al$_3$Ni to determine the site that is most energetically favorable to occupy. The spin precession frequency of the daughter radioisotope, $^{111}$Cd, is what is observed using PAC. Therefore, site EFGs for Cd in Al$_3$Ni are calculated and compared with QI signals observed in PAC.
4.2 Crystal Structure

Figure 4.1: Crystal structure of Al$_3$Ni shown with Ni-atoms in blue, Al(1)-atoms in grey and Al(2) atoms in white.

Al$_3$Ni has the orthorhombic $D0_{20}$ structure, shown in Fig. 4.1, with 16 atoms in the unit cell: four Ni-atoms and 12 Al-atoms [44]. The positions of atoms in Al$_3$Ni are listed in Table 4.1 [45, 46]. Since there are different atomic surroundings, there are two inequivalent Al-sites, denoted Al(1) and Al(2). Each Ni atom has nine Al-atom nearest-neighbors ($nn$): three Al(1)- and six Al(2)-type atoms. Each type of Al-site has three $nn$ Ni-atom.
Table 4.1: Internal atom positions determined by X-ray diffraction for Al$_3$Ni. Positions are given in units of lattice parameters $a$, $b$, and $c$ [44-46]. Note: The $y$-coordinates for Al(1) and Ni atoms are fixed at 0.25 by symmetry.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>4c</td>
<td>0.011</td>
<td>0.250</td>
<td>0.415</td>
</tr>
<tr>
<td>Al(2)</td>
<td>8d</td>
<td>0.174</td>
<td>0.053</td>
<td>0.856</td>
</tr>
<tr>
<td>Ni</td>
<td>4c</td>
<td>0.869</td>
<td>0.250</td>
<td>0.945</td>
</tr>
</tbody>
</table>

4.3 PAC Results

Fig. 4.2 shows PAC spectra for samples of Al-Ni alloys having nominal compositions of 23.2, 25.4, 27.5 and 33.1 at% Ni. For Ni-rich samples, indium was observed to occupy one of the two Al-sites, as observed by a prominent quadrupole interaction with fundamental frequency $\omega_1 = 263.0$ (1) Mrad/s and electric field gradient asymmetry parameter $\eta = 0.78(2)$ (see Fig. 4.2). The “beating” observed over a time of 125 ns arises from interference between harmonics having similar frequencies $\omega_1$ and $\omega_2$. For the Ni-poor sample (top), the spectrum predominantly exhibited an ill-defined quadrupole interaction that is attributed to indium being located in grain boundaries or similar irregular sites that have a great multiplicity of local atomic configurations and, consequently, electric field gradients.
Figure 4.2: PAC spectra for Al₃Ni at room temperature as a function of composition showing a prominent QI signal with \( \omega_1 = 263.0 \) (1) Mrads/s and \( \eta = 0.78(2) \). In-probes on grain boundaries appear as a “glitch” in the time-domain spectra and as a broad “hump” centered at 175 Mrads/s in the frequency-domain spectrum (top right) [47].

4.4 DFT Results

The FP-(L)APW+lo method was employed to calculate structural and electronic properties of Al₃Ni fully-relaxed unit cells. All Al₃Ni DFT calculations presented here involved unit cells containing 16 atoms. For calculations of In-site enthalpies and Cd-site EFGs, one host atom was replaced by a solute atom so that the concentration of solutes was 6.25 at.%. The exchange and correlation effect was treated using GGA (PBE) [27]. Inside the muffin-tin spheres, the wave functions, the electron charge densities and the potentials were expanded in terms of spherical harmonics up to angular momenta
\( l_{\text{max}} = 10 \). In the interstitial region they were expanded in plane waves to a cutoff \( R_{MT}K_{\text{max}} = 9 \). For Al, Ni and In atoms, \( R_{mi} \) values 2.04, 2.3 and 2.17 bohr respectively were used. The number of special \( k \)-points used in the irreducible Brillouin zone was 88. The SCF iteration process was repeated until the calculated total energy of crystal converged to better than 0.1 mRy for site energy calculations. For EFG calculations, the SCF process was repeated until the calculated total energy of the crystal converged to better than 0.1 mRy and the integrated charge density to better than 1.0 \( e \).

Calculations were optimized with respect to lattice volume, \( b/a \) and \( c/a \) ratios, and additionally with respect to atomic coordinates that are not bound by symmetry. A comparison of optimized lattice parameters and measured values is given in Table 4.2. The optimized lattice parameters agree well with parameters determined by X-ray diffraction [46]. Optimized volume is 1.5% smaller than the measured value. Ratios \( b/a \) and \( c/a \) are respectively, are 0.8% smaller and 1.4% greater than measured values.

Table 4.2: Comparison of optimized and measured lattice parameters (Å) of Al₃Ni.

<table>
<thead>
<tr>
<th></th>
<th>DFT</th>
<th>X-Ray [46]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>6.5650</td>
<td>6.6114</td>
</tr>
<tr>
<td>( b )</td>
<td>7.2570</td>
<td>7.3662</td>
</tr>
<tr>
<td>( c )</td>
<td>4.8450</td>
<td>4.8112</td>
</tr>
<tr>
<td>( b/a )</td>
<td>1.1054</td>
<td>1.1142</td>
</tr>
<tr>
<td>( c/a )</td>
<td>0.7380</td>
<td>0.7277</td>
</tr>
<tr>
<td>( V )</td>
<td>230.826</td>
<td>234.310</td>
</tr>
</tbody>
</table>
Relaxed atom positions are given in Table 4.3. Internal atomic positions were determined by minimizing forces on atoms in an optimized unit cell. Relaxed atom positions are in excellent agreement with values measured using X-ray diffraction. Overall, DFT calculations reproduced the experimentally determined structure well.

Table 4.3: DFT calculated relaxed atom positions in Al$_3$Ni given in units of lattice parameters $a$, $b$ and $c$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>4c</td>
<td>0.013</td>
<td>0.250</td>
<td>0.415</td>
</tr>
<tr>
<td>Al(2)</td>
<td>8d</td>
<td>0.172</td>
<td>0.051</td>
<td>0.85</td>
</tr>
<tr>
<td>Ni</td>
<td>4c</td>
<td>0.867</td>
<td>0.250</td>
<td>0.945</td>
</tr>
</tbody>
</table>

Fig. 4.3 shows nearest-neighbors for the three sites. Using relaxed atom positions, average distances between lattice sites and nearest-neighbors with either host atoms or solute atoms occupying the lattice sites were obtained and are given in Table 4.4. For pure Al$_3$Ni, each type of Al-atoms are surrounded by three Ni-$nn$ at distances ranging from 2.460 - 2.732 Å for Al(1) and 2.410 - 2.498 Å for Al(2). Whereas Ni has a total of nine Al-$nn$ (three Al(1)-$nn$ and six Al(2)-$nn$) at an average distance of 2.477 Å.
Figure 4.3: Al-sites (left) and Ni-site (right) nearest-neighbors in Al$_3$Ni are indicated by connecting lines. Al(1)-atoms are white, Al(2)-atoms are grey and Ni-atoms are in blue. Nearest-neighbor distances are shown for the three sites.

As can be seen in Table 4.4, all average \( nn \)-distances increased when In-solutes or Cd-solutes occupied the sites. For Cd-solutes on either the Al(1)- or Al(2)-site, average \( nn \)-distances increased by 0.002 Å. Whereas for In-solutes on Al(1)- or Al(2)-sites, the average \( nn \)-distance increased by 0.033 and 0.076 Å, respectively. Average \( nn \)-distances increased by 0.163 and 0.131 Å, respectively when either In-solutes or Cd-solutes occupied Ni-sites.
Table 4.4: Average distance $D$ between lattice site and its nearest-neighbors in Al$_3$Ni with host atoms or with solutes X (= Cd or In) occupying Al(1)-, Al(2)- and Ni-sites.

<table>
<thead>
<tr>
<th>site - nn</th>
<th>Average interatomic distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D[X_{Al(1)} - Ni]$</td>
<td>host 2.546 Cd 2.548 In 2.579</td>
</tr>
<tr>
<td>$D[X_{Al(2)} - Ni]$</td>
<td>host 2.442 Cd 2.444 In 2.518</td>
</tr>
<tr>
<td>$D[X_{Ni} - Al]$</td>
<td>host 2.477 Cd 2.608 In 2.640</td>
</tr>
</tbody>
</table>

Calculated electric field gradients and asymmetry parameters for Cd and site enthalpies for In substituting inequivalent sites in Al$_3$Ni are listed in Table 4.5. Calculated EFG values for Cd at Al(1), Al(2) and Ni-sites are respectively, $V_{zz} = +12.95, -12.12$ and $+2.34 \times 10^{21}$ V/m$^2$. Calculated asymmetry parameters were $\eta = 0.93$ at both inequivalent Al-sites and $\eta = 0.60$ at the Ni site. Calculated asymmetry parameters and $|V_{zz}|$ values for the two inequivalent Al-sites are both close to the measured values $|V_{zz}| = 13.5 \times 10^{21}$ V/m$^2$, $\eta = 0.78(2)$.

Site enthalpies for In occupying Al- or Ni-sites in Al$_3$Ni are given by

$$E_n = E[In_{Al(n)}] + E[Al] - E[In] - E_o \quad (n = 1, 2) \quad (4.1)$$

$$E_{Ni} = E[In_{Ni}] + E[Ni] - E[In] - E_o, \quad (4.2)$$

where $E_{Ni}$ and $E_n$ represent the site enthalpies of the system when In substitutes Ni or either of the two inequivalent Al($n$)-sites ($n = 1, 2$), respectively. $E[In_{Al(n)}]$ and $E[In_{Ni}]$ are the total energies of the 1x1x1 unit cell with In on Al($n$)- or In on Ni-sites. $E[Al], E[In], E[Ni]$ are the total energies of metals in their respective lattices and $E_o$ is the total
energy of $\text{Al}_3\text{Ni}$ with no defects. Enthalpy differences between Al- and Ni-sites depend on reference states of elements (i.e. elemental solids or gaseous state) but differences between Al-sites does not. Site enthalpies for In substituting for Al(1), Al(2) and Ni are respectively, 0.89, 1.24, 4.76 eV.

For inequivalent sites Al(2) and Al(1) in the ideal $\text{Al}_3\text{Ni}$ structure, the situation is that of a two-state thermodynamic system and the site-fraction ratio is expressed as

$$f_2 \over f_1 = \frac{2e^{\frac{-G_2}{k_BT}}}{e^{\frac{-G_1}{k_BT}}} = 2e^{\left(\frac{S_2-S_1}{k_B}\right)} \cdot e^{\left(-\frac{(H_2-H_1)}{k_BT}\right)}$$ \hspace{1cm} (4.2)

in which the factor of 2 accounts for the 2:1 ratio of the number of sites and $G_n = H_n - TS_n$ is the free energy of the solute on site $n$, that can be expressed in terms of the enthalpy $H_n$ and vibrational entropy $S_n$. Inserting the DFT calculated site enthalpies $E_1$ and $E_2$ into Eq. 4.2 for $H_1$ and $H_2$ and taking $S_2 - S_1 = 0$ yields $f_2/f_1 = 0.001$ at $T = 500$ K. Thus, it is impossible to observe In occupying Al(2)-sites. As such, the observed QI signal is attributed to probes on the Al(1)-site.
Table 4.5: Calculated site enthalpies for In and calculated and measured EFG values for Cd in Al\textsubscript{3}Ni.

| Site | $E$ (eV) | $V_{zz}$ ($10^{21}$ V/m$^2$) | $\eta$ | $|V_{zz}|$ ($10^{21}$ V/m$^2$) | $\eta$ |
|------|----------|-------------------------------|-------|-------------------------------|-------|
| Al(1) | 0.89 | 12.95 | 0.93 | 13.58(1) | 0.78(2) |
| Al(2) | 1.24 | -12.12 | 0.93 | | |
| Ni | 4.76 | -2.34 | 0.60 | | |

4.5 Discussion

Site preference for indium solutes in Al\textsubscript{3}Ni was determined through PAC measurements and DFT calculations. PAC measurements revealed that for Ni-rich samples, indium preferred to occupy one of the two Al-sites, as observed by a prominent quadrupole interaction with fundamental frequency $\omega_1 = 263.0(1)$ Mrad/s and asymmetry parameter $\eta = 0.78(2)$ (see Fig. 4.2). For the Ni-poor sample, indium preferred to locate in grain boundaries.

DFT calculated values of the electric field gradient and asymmetry parameter for Cd occupying either of the Al-sites are both approximately equal to the measured values. Thus, one cannot determine which site Cd prefers to occupy based on EFGs alone. However, as seen in Table 4.6 the site enthalpy for In on a Ni-site is approximately 3.5 eV higher than for In on either of the two inequivalent Al-sites. This indicates that In solutes in Al\textsubscript{3}Ni prefer to occupy Al-sites that are surrounded by three Ni-$nn$ rather than Ni-sites surrounded by nine Al-$nn$. Additionally, it was shown that nearest-neighbor distances increased the most for In/Cd solutes on Ni-sites, and that lattice disorder was small when either Cd- or In-solutes occupied Al-sites. Furthermore, the increase in the average $nn$-distance was smallest when an In-solute occupied the Al(1)-site.
The site enthalpy for In on Al(1)-site is 0.35 eV lower than the Al(2)-site, indicating that it is more energetically favorable for In to occupy Al(1)-sites, explaining the observation of a single predominate QI signal. For Al$_3$Ni, site preference of In is only observable experimentally as a function of composition.

In the present Al$_3$Ni study and in the Ni$_2$Al$_3$ study [6], site preference of In solutes was studied only as a function of composition. Systems where site preference is a function of only temperature, Al$_3$Ti and Al$_3$Zr [8], and of both temperature and composition, GdAl$_2$ [7], are discussed in the next chapter.
Chapter 5: Al\textsubscript{3}Ti and Al\textsubscript{3}Zr

5.1 Introduction

Site fractions of \textsuperscript{111}In/Cd impurity probe atoms occupying two inequivalent Al-sites in Al\textsubscript{3}Ti and Al\textsubscript{3}V ($D0_{22}$) and three inequivalent Al-sites in Al\textsubscript{3}Zr ($D0_{23}$) were measured at various temperatures ranging from 600 to 1,210 K using PAC [8]. Sites were identified via characteristic nuclear quadrupole interactions. For all three phases, a single axially symmetric quadrupole interaction signal dominated at low temperature and was attributed to probes on the Al(2)-site. At high temperature, small site fractions of additional signals were observed. These new signals were attributed to probes transferring among inequivalent Al-sites and appeared and disappeared reversibly as temperature was increased and decreased.

In a previous study, the site preference of \textsuperscript{111}In impurities in the Laves phase GdAl\textsubscript{2} was studied as a function of composition and temperature [7]. Occupied Gd- and Al-sites were determined through measurements of quadrupole interactions using PAC. In that study, 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 via the reaction $\text{In}_{\text{Gd}} + \text{Al}_{\text{Al}} \leftrightarrow \text{In}_{\text{Al}} + \text{Al}_{\text{Gd}}$. Applying the law of mass action to the reaction leads to

$$\frac{[\text{In}_{\text{Al}}][\text{Al}_{\text{Gd}}]}{[\text{In}_{\text{Gd}}][\text{Al}_{\text{Al}}]} = \exp \left( - \frac{G_{\text{fr}}}{k_B T} \right)$$

(5.1)
in which $G_{tr}$ is the free energy of transfer and square brackets represent mole fractions of atoms on the respective sublattices indicated by subscripts. The mole fraction of Al-sites occupied by Al-atoms [$Al_{Al}$] is equal to 1 for dilute defect concentrations. Eq. 5.1 can be written in terms of the ratio of measured fractions of probes on the two sites:

$$\frac{f_{Gd}}{f_{Al}} = \frac{[In_{Gd}]}{2[In_{Al}]} = [Al_{Gd}] \exp\left(-\frac{G_{tr}}{k_BT}\right).$$  \hfill (5.2)

The factor of 2 accounts for the 2:1 ratio of sites on the Al- and Gd-sublattices. The site-fraction ratio depends on sample composition through the antisite mole fraction [$Al_{Gd}$]. As such, it is not possible to determine the difference of site-enthalpies of $In_{Gd}$ and $In_{Al}$ from an overall fitted activation enthalpy without making additional assumptions or approximations about the mole fraction of $Al_{Gd}$ defects.

The situation is much simpler for $Al_3Ti$ and $Al_3Zr$ crystal structures that exhibit a solute site transfer among inequivalent sites of the same element. For example, in either phase the transfer reaction $In_{Al(2)} + Al_{Al(1)} \leftrightarrow In_{Al(1)} + Al_{Al(2)}$ no longer involves an intrinsic defect such as $Al_{Gd}$. Therefore, the site-fraction ratio is independent of composition and the free energy of transfer is simply equal to the difference between enthalpies of the solute atom on the two sites.

Ratios of site fractions were fitted with thermally activated expressions, yielding differences in vibrational entropies and site enthalpies. Enthalpy differences were greatest for $Al_3Zr$, 0.21(1) and 0.24(2) eV, and smaller for $Al_3Ti$, 0.075(17), and $Al_3V$, 0.023(4) eV. Vibrational entropy differences were small ranging from 0 to -0.20 $k_B$. 

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While calculations for this work were in progress, Wodniecki et al. [48] reported DFT calculations performed to assign the observed QI signal to the possible lattice sites in Al$_3$Ti. They calculated EFGs using 2x2x1 supercells with $R_{MT}K_{\text{max}} = 8.5$ and 2176 $k$-points and GGA(PBE) [27] for Cd occupying Al(1)-, Al(2)- and Ti-sites to be $+7.5$, $-5.7$ and $-3.5 \times 10^{21}$ V/m$^2$. Through comparison of the measured ($|V_{ZZ}| = 5.0(1) \times 10^{21}$ V/m$^2$) and calculated EFGs, they established that Cd probes settled at the Al(2)-site, in agreement with earlier attributions from PAC measurements [8] [49].

In this work, DFT calculations were performed to gain a better understanding of the site preference behavior observed in phases having the related $D0_{22}$ and $D0_{23}$ tetragonal crystal structures. Site electric field gradients were calculated for Cd atoms substituting all possible lattice sites in Al$_3$Ti and Al$_3$Zr as in work on Al$_3$Ti by Wodniecki et al. Additionally, site enthalpies were calculated for In impurities occupying the possible sites. Calculated site EFGs and site enthalpies were compared to observed QI signals and measured enthalpy differences.
Figure 5.1: Crystal structures $D_{0_{22}}$ (left) and $D_{0_{23}}$ (right). $TM$-, $Al(1)$-, $Al(2)$- and $Al(3)$-sites are indicated respectively by blue, black, grey and white atoms.

Unit cells of the $Al_3Ti$ (left) and the $Al_3Zr$ (right) structures are shown in Fig. 5.1. Both are tetragonal with one site for the transition-metal ($TM$) element and, respectively, two or three sites for the Group III element [44]. Both structures are composed of alternating stacks of mixed planes of $TM$- and $Al$-atoms and full planes of $Al$-atoms, with the difference between the two structures related to offsets between neighboring mixed planes that are transverse to the tetragonal (vertical) axis.
The local environments of each site are illustrated in Fig. 5.2. In both Al₃Ti and Al₃Zr, the axially symmetric TM-sites are surrounded by 12 Al-atoms. Al(1)-sites are surrounded by four TM-near-neighbors arranged in a square and Al(2)-sites are surrounded by four TM-nn arranged in a distorted tetrahedron. Both Al(1)- and Al(2)-sites are axially symmetric and have EFG axes aligned along the tetragonal axes. Al₃Zr has, in addition to Al(1)- and Al(2)-sites, a third Al(3)-site which is surrounded by four TM-nn arranged in a square which is nonaxial with respect to the c-axis.

Figure 5.2: Configurations of atoms neighboring the four sites (red) in Al₃Ti and Al₃Zr structures are shown with TM- and Al-sites indicated respectively by blue and grey atoms. The tetragonal crystal axis is oriented vertically in the diagrams.

5.3 PAC Results

Earlier PAC studies of ¹¹¹In probes in Al₃Ti were performed by Lauer et al. [49] and in Al₃Zr by Wodniecki et al. [50]. In Ref. [50], a single axially symmetric QI signal (|V_{zz}| = 4.31 \times 10^{21} \text{ V/m}^2, \eta = 0) was observed and attributed to ¹¹¹In probes occupying Zr-sites. A PAC spectrum in Ref. [49] showed a single axially symmetric QI signal (|V_{zz}| = 5.0 \times 10^{21} \text{ V/m}^2, \eta = 0). Taking into account the different atomic radii of In, Ti, and Al
(1.55Å for In, 1.40Å for Ti, and 1.25Å for Al [51]), it was suggested [49] that indium replaces aluminum atoms in Al₃Ti but is located only on the Al(2)-site because of larger distances to the neighboring Ti atoms as compared to the Al(1)-site. However, the large In-impurity on a Ti-site would be surrounded by 12 smaller Al-atoms. The solid solubility of In in pure Al-metal has been measured to be only at the part-per-million level at elevated temperature [43]. This strongly suggests 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. Furthermore, as in the extensive study of site preferences of indium solutes in Ni₂Al₃ phases [6] discussed in Chapter 4, solutes prefer to occupy grain-boundary sites rather than to be surrounded by nine Al-atoms in the first neighbor shell.

Temperature dependence of site preference of indium impurity atoms in Al₃Ti, Al₃V and Al₃Zr was reported in Ref. [8]. Representative time-domain and Fourier spectra for measurements on Al₃Zr are shown for three temperatures in Fig. 5.3. For all three phases one axially symmetric QI signal dominated at low temperature and was attributed to In on the Al(2)-site because of the smaller value of its EFG. As can be seen in Fig. 5.3 (right), the amplitudes of the three frequency components deviate strongly from the proportions 13:10:5 predicted when polycrystalline texture is random (refer to Eq. 2.14). The enhancement of the amplitude of the second harmonic is attributed to inhomogeneous crystallization following arc-melting. As temperature was increased, small site-fractions of additional signals were observed. This is shown for Al₃Zr at 1210 K in Fig. 5.3 (right), with two signals attributed to indium at Al(1)- and Al(3)-sites.
Since the EFG’s for sites Al(1) and Al(2) have parallel main principal axes, they must have proportional harmonic amplitudes. However, the main principal EFG axis for site Al(3) is not parallel to the c-axis and consequently the harmonic amplitudes should differ. Accordingly, 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).

Figure 5.3: PAC spectra for Al$_2$Zr along with their Fourier Transforms measured at increasing temperature [8].
In order to compare EFGs calculated at $T = 0$ K using DFT with experiment values, EFGs measured at different temperatures were extrapolated to $T = 0$ K. An experimentally well-documented feature of EFGs in metals is the temperature dependence of $V_{zz}$. The temperature dependence for most cases follows the relation [52-54]:

$$V_{zz}(T) = V_{zz}(0)(1 - BT^\alpha).$$

(5.3)

$B$ is a positive constant ranging from $10^{-4}$ to $10^{-5}$ K$^{-\alpha}$ and $\alpha$ is 3/2 over a considerable part of the temperature range. For transition metals, smaller values of $\alpha$ can occur and a fit with Eq. 5.3 is not always possible [55, 56]. For rare earth [57] and actinide [58] systems, $\alpha = 1$ is frequently found. Additionally, when the probe atom does not occupy well-defined lattice positions, anomalous values of $\alpha$ can occur [53].

The temperature dependence of the site EFGs in $\text{Al}_3\text{Ti}$ and $\text{Al}_3\text{Zr}$ were fitted to Eq. 5.3 and are shown in Fig. 5.4.
For $\text{Al}_3\text{Ti}$ and $\text{Al}_3\text{Zr}$, the temperature dependence of the EFG at the Al(1) site is linear, $\alpha \sim 1.0$. For the Al(2) site in $\text{Al}_3\text{Ti}$, a value of $\alpha = 1.19$ was obtained. In $\text{Al}_3\text{Zr}$, the temperature dependence of the EFG at the Al(2) site was found to be linear in agreement with measurements in ref. [59]. However, fitted $B$ and $\alpha$ values for the EFG temperature dependence at Al(3) in $\text{Al}_3\text{Zr}$ are much higher than what is generally found. Fitted parameters are listed in Table 5.1.
Table 5.1: Fitted parameters of the EFG temperature dependence for Al-poor Al$_3$Ti and Al$_3$Zr.

<table>
<thead>
<tr>
<th>Site</th>
<th>$V_{zz}(0)$</th>
<th>$B \text{ (K}^{-\alpha})$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_3$Ti</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(1)</td>
<td>6.10(5)</td>
<td>$7.8(9) \times 10^{-05}$</td>
<td>1.03(16)</td>
</tr>
<tr>
<td>Al(2)</td>
<td>5.14(1)</td>
<td>$4.1(6) \times 10^{-05}$</td>
<td>1.19(2)</td>
</tr>
<tr>
<td>Al$_3$Zr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(1)</td>
<td>6.65(3)</td>
<td>$5.9(9) \times 10^{-05}$</td>
<td>1.04(9)</td>
</tr>
<tr>
<td>Al(2)</td>
<td>4.30(1)</td>
<td>$8.2(9) \times 10^{-05}$</td>
<td>1.00(2)</td>
</tr>
<tr>
<td>Al(3)</td>
<td>7.11(5)</td>
<td>$8.0(2) \times 10^{-09}$</td>
<td>2.23(10)</td>
</tr>
</tbody>
</table>

For solute transfer between sites occupied by different elements, site-fraction ratios are a function not only of the difference between free energies of the solute on the two sites but also of the mole fraction and free energy of an intrinsic defect such as a vacancy or antisite atom [6] as discussed in Section 5.1. For inequivalent sites of the same element, the ratio of solute site fractions between a pair of sites is given by a simpler expression that only involves the free energies of the solute on each site [6]. Consider inequivalent sites Al(2) and Al(1) in the ideal Al$_3$Ti structure, for which the relative numbers of sites are 2:1. The situation is that of a two-state thermodynamic system, with site-fraction ratio given by

$$\frac{f_2}{f_1} = \frac{2 \exp \left( \frac{-G_2}{k_B T} \right)}{\exp \left( \frac{-G_1}{k_B T} \right)} = 2 \exp \left( \frac{(S_2 - S_1)}{k_B T} \right) \cdot \exp \left( \frac{(H_2 - H_1)}{k_B T} \right) \quad (5.4)$$

in which $G_n = H_n - TS_n$ is the free energy of the solute on site $n$, that can be expressed in terms of the enthalpy $H_n$ and vibrational entropy $S_n$. 

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Entropy and enthalpy differences in Eq. 5.4 can be determined from the intercept and slope of an Arrhenius plot of site fraction ratios measured at different temperatures. Fig. 5.5 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 Al$_3$Ti and Al$_3$V, 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:

$$\frac{f_2}{2f_1} = \exp \left( \frac{\Delta S}{k_B} \right) \exp \left( -\frac{\Delta H}{k_BT} \right),$$

with fitted enthalpy differences, $\Delta H$, given in the figure.
Figure 5.5: Arrhenius plot of measurements of site-fraction ratios as a function of temperature for Al$_3$Zr, Al$_3$Ti and Al$_3$V with fitted enthalpy differences [8].

The $T = \infty$ intercepts and slopes of fits of ratios in Fig. 5.5 give differences in vibrational entropy and enthalpy for each pair of sites. Fitted results for Al$_3$Ti, Al$_3$V and Al$_3$Zr are listed in Table 5.2. Fitted enthalpy differences between indium on site Al(1) or Al(3) and site Al(2) in Al$_3$Zr 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$_3$Ti and +0.023(4) eV for Al$_3$V. Vibrational entropy differences between sites Al(1) and Al(2) for Al$_3$Ti, Al$_3$V and Al$_3$Zr ranged from 0 to -0.20 k$_B$. For Al$_3$Zr, vibrational entropy differences between sites Al(3) and Al(2) was found to be +0.929(20) k$_B$. PAC
measurements on Al$_3$Ti and Al$_3$Zr with $^{111}$In probes indicate the indium solute location in Al-sublattice with strong preference of Al(2)-site.

Table 5.2: Fitted entropy and enthalpy differences of Arrhenius plots for Al$_3$Ti, Al$_3$V and Al$_3$Zr[8].

<table>
<thead>
<tr>
<th>Phase</th>
<th>$H_1 - H_2$ (eV)</th>
<th>$S_1 - S_2$ (k$_B$)</th>
<th>$H_3 - H_2$ (eV)</th>
<th>$S_3 - S_2$ (k$_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_3$V</td>
<td>+0.023(4)</td>
<td>-0.20(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_3$Ti</td>
<td>+0.075(17)</td>
<td>-0.13(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_3$Zr</td>
<td>+0.21(1)</td>
<td>-0.01(13)</td>
<td>+0.24(2)</td>
<td>+0.92(18)</td>
</tr>
</tbody>
</table>

5.4 DFT Results

In the present work ab initio calculations were performed to compare site energy differences for In impurities and site EFGs for Cd impurities occupying the possible sites in Al$_3$Ti and Al$_3$Zr. The structural parameters of the crystal lattices - including lattice volumes, $c/a$ ratios, and internal atomic positions when not determined by symmetry - were determined by force minimization.

The FP-(L)APW+lo method was employed to calculate the structural and electronic properties of 2x2x1 Al$_3$Ti and 2x1x1 Al$_3$Zr fully-relaxed supercells. Size of supercells were chosen so that solute concentration was 3.125 at.% for both Al$_3$Ti and Al$_3$Zr. Exchange and correlation effects were treated using GGA (PBE) [27]. Inside the muffin-tin spheres, the wave functions, the electron charge densities and the potentials were expanded in terms of spherical harmonics up to angular momenta $l_{\text{max}}=10$. In the
interstitial region they were expanded in plane waves with cutoff $R_{MT} K_{MAX} = 10$. For Al$_3$Ti, $R_{MT}$ values of 2.35 bohr for aluminum and 2.5 bohr for titanium were used. For Al$_3$Zr, $R_{MT}$ values of 2.5 bohr were used for both aluminum and zirconium. For total energy calculations the number of special $k$-points used in the irreducible Brillouin zone for Al$_3$Ti and Al$_3$Zr are 63 and 88, respectively. For site enthalpies, the SCF iteration process was repeated until the calculated total energy of crystal converged to less than 0.1 mRy. For EFG calculations, the SCF iteration process was repeated until the calculated charge density and total energy of the crystal converged to less than 1.0 e and 0.1 mRy, respectively.

Energy calculations were optimized with respect to all possible structural degrees of freedom. For the $D_{022}$ structure, energy was optimized with respect to lattice volume and $c/a$ ratio and in $D_{023}$ additionally with respect to two atomic displacements $z$(Al) and $z$(Zr) since the atomic coordinates are not bound by symmetry (Wyckoff positions 4e for $D_023$ spacegroup $I4/mmm$). Calculated and measured values for lattice parameters (and atomic displacements) are listed in Table 5.3. Calculated and measured lattice parameters are in excellent agreement. For Al$_3$Ti, calculated lattice volume was slightly less (by about 1%) than lattice volume measured at room temperature (RT) using X-ray diffraction [60] and optimized $c/a$ ratio was slightly greater (less than 1%). For Al$_3$Zr, optimized volume was 1.5% greater than the volume measured by neutron diffraction at 12 K [61] and the $c/a$ ratio is in excellent agreement. Optimized internal atomic coordinates for Al and Zr atoms were 0.1% less and 20% greater than neutron diffraction measurements for $z$(Al) and $z$(Zr) respectively.
Table 5.3: A comparison of calculated and experimental lattice parameters (Å) for Al₃Ti (D₀₂₂) and Al₃Zr (D₀₂₃) and atomic displacements for Al₃Zr. Normalized lattice parameters \( c' = c/2 \) for Al₃Ti and \( c' = c/4 \) for Al₃Zr. Normalized volumes are calculated using \( V' = a^2 \cdot c' \).

<table>
<thead>
<tr>
<th></th>
<th>Al₃Ti</th>
<th>Al₃Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>RT[^a]</td>
</tr>
<tr>
<td>( a )</td>
<td>3.8458</td>
<td>4.0201</td>
</tr>
<tr>
<td>( c' )</td>
<td>4.3067</td>
<td>4.3325</td>
</tr>
<tr>
<td>( c'/a )</td>
<td>1.1198</td>
<td>1.0777</td>
</tr>
<tr>
<td>( V' )</td>
<td>63.697</td>
<td>70.018</td>
</tr>
<tr>
<td>( z(Al) )</td>
<td>-</td>
<td>0.3747</td>
</tr>
<tr>
<td>( z(Zr) )</td>
<td>-</td>
<td>0.1191</td>
</tr>
</tbody>
</table>

\[^a\] X-ray diffraction from Ref. [60]
\[^b\] Neutron diffraction from Ref. [61]

To understand the extent of influence that site-volume has on the site preference of indium solutes in Al₃Ti and Al₃Zr, changes in site-volume due to indium or cadmium solute occupation were calculated using a crystal structure visualization program called VESTA[62]. In this work, site-volume is defined as the volume of a polyhedron centered at the lattice site of interest with nearest-neighbor sites at the vertices. Polyhedra surrounding Al(1)-, Al(2)-, Al(3)- and TM-sites in Al₃Ti and Al₃Zr are shown in Fig. 5.6, and corresponding volumes and changes in volumes due to Cd- and In-atoms occupying the sites are listed in Table 5.4.
Site-volumes were calculated using DFT optimized lattice parameters. For host atoms occupying the sites in Al$_3$Ti, all site-volumes were found to be $V_0 = 44.775$ Å$^3$. However, for host atoms occupying sites in Al$_3$Zr, site-volumes were: smallest for the Al(3)-site at $V_0 = 57.217$ Å$^3$, equal for the Al(1)- and Zr-sites at $V_0 = 58.347$ Å$^3$, and largest for the Al(2)-site at $V_0 = 60.065$ Å$^3$. Site-volumes increased the most for In-solutes occupying sites in both Al$_3$Ti and Al$_3$Zr. For Al$_3$Ti, the change in site-volume for In on either of the Al-sites was approximately half that of the Ti-site. This indicates that the In-atom disorders the Al$_3$Ti lattice the least when it’s on either of the Al-sites. However, the change in site-volume for In occupying sites in Al$_3$Zr was smallest for the Zr-site, indicating that lattice disorder is minimum when In occupies the Zr-site.
Table 5.4: Site-volumes for host atoms ($V_0$) at sites in Al$_3$Ti and Al$_3$Zr and increases in site-volume due to Cd- or In-atoms occupying the sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>$V_0$ (Å$^3$)</th>
<th>$\Delta V$ (Cd-impurity)</th>
<th>$\Delta V$ (In-impurity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_3$Ti</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(1)</td>
<td>44.775</td>
<td>2.22</td>
<td>2.39</td>
</tr>
<tr>
<td>Al(2)</td>
<td>44.775</td>
<td>1.40</td>
<td>2.31</td>
</tr>
<tr>
<td>Ti</td>
<td>44.775</td>
<td>4.21</td>
<td>4.42</td>
</tr>
<tr>
<td>Al$_3$Zr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(1)</td>
<td>58.347</td>
<td>2.24</td>
<td>3.07</td>
</tr>
<tr>
<td>Al(2)</td>
<td>60.065</td>
<td>2.10</td>
<td>3.44</td>
</tr>
<tr>
<td>Al(3)</td>
<td>57.217</td>
<td>1.60</td>
<td>2.98</td>
</tr>
<tr>
<td>Zr</td>
<td>58.347</td>
<td>1.93</td>
<td>2.62</td>
</tr>
</tbody>
</table>

To help determine the origin of the QI signals (Fig. 5.2) observed in Al$_3$Ti and Al$_3$Zr, EFGs were calculated at Cd impurities. Measured and calculated values for EFGs and corresponding asymmetry parameters at Cd impurities in Al$_3$Ti and Al$_3$Zr are given in Table 5.5. Site EFGs in Al$_3$Ti and Al$_3$Zr were calculated using 63 $k$-points and $R_{MTK_{MAX}} = 8.0$ for Al$_3$Ti and 88 $k$-points and $R_{MTK_{MAX}} = 8.0$ for Al$_3$Zr. For EFG calculations, the self-consistency was achieved by demanding the convergence of the integrated charge difference between the last two iterations to be smaller than $10^{-3}$ electron.
Table 5.5: Comparison between the measured (extrapolated to $T = 0$ K) and calculated EFG values and asymmetry parameters at probe sites in units of $10^{21}$ V/m$^2$ for Al$_3$Ti and Al$_3$Zr.

<table>
<thead>
<tr>
<th>Site</th>
<th>DFT</th>
<th>DFT (Ref. [48])</th>
<th>PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_{zz}$</td>
<td>$V_{zz}$</td>
<td>$</td>
</tr>
<tr>
<td>Al(1)</td>
<td>7.80</td>
<td>7.5</td>
<td>6.10(5)</td>
</tr>
<tr>
<td>Al(2)</td>
<td>-6.29</td>
<td>-5.7</td>
<td>5.14(1)</td>
</tr>
<tr>
<td>Ti</td>
<td>-3.78</td>
<td>-3.5</td>
<td>-</td>
</tr>
<tr>
<td>Al(1)</td>
<td>8.87</td>
<td>0.03</td>
<td>6.65(3)</td>
</tr>
<tr>
<td>Al(2)</td>
<td>-5.24</td>
<td>0.22</td>
<td>4.30(1)</td>
</tr>
<tr>
<td>Al(3)</td>
<td>9.69</td>
<td>0.07</td>
<td>7.11(5)</td>
</tr>
<tr>
<td>Zr</td>
<td>3.26</td>
<td>0.53</td>
<td>-</td>
</tr>
</tbody>
</table>

For Al$_3$Ti, calculated EFG values for Cd impurities on Al(1), Al(2) and Ti sites were respectively $+7.8$, $-6.29$ and $-3.78 \times 10^{21}$ V/m$^2$. Calculated values for $\eta$ at these sites were calculated to be less than 0.01. Calculated EFG values at the Al(1) and Al(2) sites are respectively $1.7$ and $1.1 \times 10^{21}$ V/m$^2$ greater than values determined at $T = 0$K from fitted temperature dependence of measured EFGs (refer to Table 5.1). In a previous study made by Wodniecki et al [48], EFGs for Cd impurities in Al$_3$Ti were calculated using DFT. They used 2x2x1 supercells with $R_{mt}K_{max}=8.5$, 12 $k$-points and optimized lattice parameters of $a = 3.846\text{Å}$ and $c = 8.621\text{Å}$. EFG values calculated by Wodniecki et al [48] for Cd atoms on Al(1) and Al(2) sites were respectively $1.4$ and $0.56 \times 10^{21}$ V/m$^2$ greater than values determined at $T = 0$K from fitted temperature dependence of measured EFGs (refer to Table 5.1). Additionally, all site EFGs calculated in the present work are in good agreement with results of Wodniecki et al.
For Al₃Zr, EFGs calculated for Cd impurities on Al(1)-, Al(2)-, Al(3)- and Zr-sites were respectively +8.87, -5.24, +9.69 and +3.26 x 10²¹ V/m². Values for η at Al(1)-, Al(2)-, Al(3)- and Zr-sites were, respectively, η = 0.03, η = 0.22, η = 0.07 and η = 0.53. Calculated EFGs for Cd at Al(1)-, Al(2)- and Al(3)-sites were respectively 2.22, 0.94 and 2.58 x10²¹ V/m² greater than values at T = 0K extrapolated from temperature dependence of measured EFGs (refer to Table 5.1).

The site preference of ¹¹¹In/Cd probe atoms in Al₃Ti and Al₃Zr can be understood by comparing site enthalpies for In on Al- or the Ti-sites (Zr-sites for Al₃Zr). A smaller site enthalpy indicates that the substitution behavior is favorable. Listed in Table 5.6 are site enthalpies of the system for In substitution which are given by

\[
E_i = e[In_{Al(i)}] + e[Al] - e[Al₃TM] - e[In],
\]

\[
E_{TM} = e[In_{TM}] + e[TM] - e[Al₃TM] - e[In]
\]

where \(E_{TM}\) and \(E_i\) represent the site enthalpy of the systems when In substitutes one TM (Ti or Zr) or one of the three inequivalent Al(i)-sites (\(i = 1, 2, 3\)), respectively. Parameters \(e[In_{Al(i)}]\) and \(e[In_{TM}]\) are the energies of a supercell with In occupying an Al(i)- site or a TM-site in place of the normal host atom. The total energy of the pure Al₃TM supercell is \(e[Al₃TM]\) and \(e[Al]\), \(e[TM]\) and \(e[In]\) are the total energies of Al, \(TM\) and In atoms in respective crystal structures.
Table 5.6: Calculated site-enthalpies in units of eV for In substituting inequivalent sites in Al$_3$Ti and Al$_3$Zr.

<table>
<thead>
<tr>
<th></th>
<th>Al$_3$Ti</th>
<th>Al$_3$Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>0.96</td>
<td>$E_1$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>0.82</td>
<td>$E_2$</td>
</tr>
<tr>
<td>$E_{\text{Ti}}$</td>
<td>3.09</td>
<td>$E_3$</td>
</tr>
<tr>
<td>$E_{\text{Zr}}$</td>
<td></td>
<td>$E_{\text{Zr}}$</td>
</tr>
</tbody>
</table>

For Al$_3$Ti, $E_1 = 0.96$ eV and $E_2 = 0.82$ eV are much less than $E_{\text{Ti}} = 3.09$ eV. As for Al$_3$Zr, $E_1$, $E_2$ and $E_3$ values are 0.72, 0.51 and 0.77 eV respectively, and are much less than $E_{\text{Zr}} = 3.41$ eV. Furthermore, the site enthalpy for In on the Al(2)-site, $E_2$, is smallest for both Al$_3$Ti and Al$_3$Zr indicating In substituting an Al(2)-atom to be most favorable.

Measured and calculated enthalpy differences are compared in Table 5.7. For Al$_3$Ti, the calculated enthalpy difference $E_1 - E_2$ differs from measurement by only 0.065 eV. For Al$_3$Zr, calculated results are in better agreement with PAC measurements. The calculated enthalpy difference between In substituting Al(1)- or Al(2)-sites equals the measured value $H_1 - H_2$ and $E_2 - E_3$ is only 0.03 eV greater than the measured value $H_3 - H_2$. 

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Table 5.7: Comparison of measured (\(H\)) and calculated (\(E\)) enthalpy differences (in units of eV) in \(\text{Al}_3\text{Ti}\) and \(\text{Al}_3\text{Zr}\) phases.

<table>
<thead>
<tr>
<th></th>
<th>(H_1 - H_2)</th>
<th>(H_3 - H_2)</th>
<th>(E_1 - E_2)</th>
<th>(E_3 - E_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_3\text{Ti})</td>
<td>0.075(17)</td>
<td>-</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Al}_3\text{V})</td>
<td>0.023(4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Al}_3\text{Zr})</td>
<td>0.21(1)</td>
<td>0.24(2)</td>
<td>0.21</td>
<td>0.27</td>
</tr>
</tbody>
</table>

5.1.5 Discussion

Site fractions of \(^{111}\text{In}/\text{Cd}\) impurity probe atoms occupying either of the two inequivalent Al-sites in \(\text{Al}_3\text{Ti}\) and \(\text{Al}_3\text{V}\) and up to three inequivalent Al-sites in \(\text{Al}_3\text{Zr}\) were measured using PAC. Sites were identified via characteristic nuclear quadrupole interactions. For all three phases, a single axially symmetric quadrupole interaction signal dominated at low temperature and was attributed to In on the Al(2)-site. At high temperature, small site fractions of additional signals were observed which were attributed to In probes occupying Al(1)-sites in \(\text{Al}_3\text{Ti}\) and Al(1)- and Al(3)-sites for \(\text{Al}_3\text{Zr}\). Fitted enthalpy differences between indium on site Al(1) or Al(3) and site Al(2) in \(\text{Al}_3\text{Zr}\) were both found to be close to 0.22 eV. Enthalpy differences between In on site Al(1) and Al(2) were 0.075 eV in \(\text{Al}_3\text{Ti}\).

Density functional theory was used to calculate electric field gradients at Cd-sites and site enthalpies of atomic configurations where the Al- or the Ti-sites (Zr-sites for \(\text{Al}_3\text{Zr}\)) are occupied by In. By comparing calculated and measured EFGs, it was determined that the dominant QI signal observed at low temperature was from \(^{111}\text{In}/\text{Cd}\).
probes on Al(2)-sites for both Al$_3$Ti and Al$_3$Zr. The calculated site enthalpies of the Al$_3$Ti and Al$_3$Zr systems where In occupies Al- or TM-sites were in good agreement with experimental enthalpy differences. For Al$_3$Ti, $E_{Ti} = 3.09$ eV was much greater than $E_1 = 0.96$ eV and $E_2 = 0.82$ eV indicating that it is more likely that In to substitutes for Al rather than Ti, even at high temperature. Similar to Al$_3$Ti, it was found that in Al$_3$Zr, $E_{Zr} = 3.41$ eV was much greater than $E_1 = 0.72$ eV, $E_2 = 0.51$ eV and $E_3 = 0.77$ eV indicating that Al substitution is more likely than Zr substitution. Furthermore, the site enthalpy for In occupying the Al(2)-site is smallest for both Al$_3$Ti and Al$_3$Zr which shows that In prefers this site. This is consistent with a dominant QI signal in PAC measurements at low temperature that was earlier attributed to $^{111}$In/Cd probes on Al(2)-sites.
Chapter 6: In₃R

6.1 Introduction

Perturbed angular correlation spectroscopy was applied to study diffusion of $^{111}$In/Cd solutes in rare earth (R) indides having the $L1_2$ crystal structure. It was shown in Ref. [12] that it is possible to measure jump frequencies of PAC probe atoms in In₃La due to fluctuating EFGs at the probe nuclei produced by the jumps. This was followed up with measurements on all In₃R phases [17]. All phases appear as “line compounds” in binary phase diagrams; however, they must have a finite phase width [12]. Measurements were made for samples having compositions at opposing phase boundaries and jump frequency was found to be highly dependent on composition of the samples. Activation enthalpies were obtained by fitting jump frequencies to Arrhenius temperature dependences. Higher jump frequencies and lower activation enthalpies were observed at the more In-rich phase boundary for light-rare earth indides (La to Nd) and at the less In-rich boundary for heavy rare earth indides (Sm to Lu). This reversal of behavior strongly suggests the existence of different diffusion mechanisms.

To complement studies of rare-earth indides, three other series of $L1_2$ phases were studied: Al₃R [63], Ga₃R [64], and Sn₃R [18, 65]. Again, measurements were made at opposing phase boundary compositions. In these phases, In is no longer a host element and non-stoichiometry of the sample could drive $^{111}$In/Cd probes to occupy the sublattice of a host element whose composition is sub-stoichiometric [66]. For all aluminide and gallide phases, it was found that for R-poorer compositions the $^{111}$In/Cd probes transferred to cubic R-sites, making it impossible to measure jump frequencies on
sublattices of Al and Ga at that boundary composition. However, for all stannides In did not transfer to the R-sublattices and it was observed that jump frequencies were greater for the Sn-poor composition, in contrast with indides. Additionally, it was found that the jump frequencies in the indides differ by factors up to 10-100, but only by a factor of three in the stannides.

To gain insight into the change in diffusion mechanism between light and heavy lanthanide indides, DFT was used to calculate formation energies of defects in In$_3$La and In$_3$Lu using 2x2x2 supercells that took into account energy decreases associated with atomic relaxation. Additionally, EFGs were calculated at Cd sites and compared with measured QI values.
6.2 Crystal Structure and point defects

Figure 6.1: The $L_1^2$ crystal structure is shown with rare earth atoms in blue and indium atoms in red. Principal axes of EFGs for probe atom (yellow) jumps are shown for adjacent In-sites.

$\text{In}_3\text{La}$ and $\text{In}_3\text{Lu}$ (denoted generically as $A_3B$ phases) have the cubic $L_1^2$ structure shown in Fig. 6.1. In the fully ordered crystal, corner positions of the unit cell (the $B$-sublattice) are occupied by $B$-atoms and face-centered positions (the $A$-sublattice) by $A$-atoms only. The $B$-site has cubic point symmetry, and the $A$-site has tetragonal symmetry. The coordination number of $B$-atoms (on the $B$-sublattice) is 12 (i.e., each $B$-atom is surrounded by 12 $A$-atoms), whereas the coordination number of $A$-atoms is 4+8 (i.e., each $A$-atom on the $A$-sublattice has 4$B$- and 8$A$-atom nearest-neighbors). There are $N_a = 3/4N_L$ $A$-sublattice sites and $N_b = 1/4N_L$ $B$-sublattice sites where $N_L$ is the total number of lattice sites.

$L_1^2$ phases appear as “line compounds” in binary phase diagrams of indium and rare earth elements [67]. This means that widths of the $L_1^2$ phase fields are narrower than the typical resolution of about 1 at.% in conventional metallurgical phase analysis.
Narrow field widths imply high formation enthalpies for point defects and, consequently, excellent ordering of elements on their respective sublattices.

Concentrations of intrinsic point defects (antisite, vacancy and interstitial) vary due to their different formation energies, and they depend on temperature and composition. For a compound of composition $A_{3+x}B_{1-4x}$, in which $x$ marks the deviation from the stoichiometric 75:25 composition, deviations from stoichiometry are accommodated by creation of constitutional (or structural) point defects. Assuming that formation energies of interstitials are much higher than those of vacancies and antisite defects as is typical for close-packed intermetallic compounds, only four types of point defects need to be considered, vacancies and antisite atoms on both sublattices. In $A$-rich ($x > 0$) or $B$-rich ($x < 0$) $A_3B$ alloys, the constitutional point defects are $V_B$ and $A_B$, or $V_A$ and $B_A$, respectively. At finite temperatures, there are additional defects due to thermal activation. Thermally activated defects have to appear in balanced combinations in order to maintain the overall composition of the alloy. Balanced defect reactions include:

\[
\text{Four-vacancy: } 0 \leftrightarrow 3V_A + V_B \quad (6.1)
\]

\[
\text{Antisite-pair: } 0 \leftrightarrow A_B + B_A \quad (6.2)
\]

\[
\text{Five-defect: } 0 \leftrightarrow 4V_A + A_B \quad (6.3)
\]

where $0$ indicates a perfect lattice. Reactions 6.1 and 6.3 occur, in effect, by removing one $A_3B$ molecule and placing it on the surface, leaving four elementary vacancies (6.1) that are assumed to be unbound. Reaction 6.3 in addition has the transfer reaction $A_A + V_B \leftrightarrow A_B + V_A$. In reaction 6.2 two antisite atoms are made by exchanging places.
The thermal equilibrium concentrations of point defects in $A_3B$ can be calculated using a thermodynamic model presented in Ref. [68]. There are two constraint conditions in an ordered $A_3B$ crystal having the $L1_2$ structure [69]. The first is that the total number of $A$- and $B$-atoms is conserved. The second is the assumption of constant composition. This leads to an equation of constraint given by

$$3[B_A] + 3\left(\frac{1}{4} - x\right)[V_A] + 4x = [A_B] + \left(\frac{3}{4} + x\right)[V_B],$$

(6.4)

where the factors in brackets represent mole fractions of the corresponding defects including antisite atoms and vacancies on the two sublattices.

In cubic structures, the diffusivity $D$ is related to the jump distance $d$ and jump frequency $w$ via

$$D = \frac{1}{6}fd^2w,$$

(6.5)

where $w$ is defined as the inverse of the mean residence time of an atom at a site, $f$ is a correlation factor such as for a vacancy diffusion mechanism, which is generally between 0 and 1 and accounts for the nonrandomness of direction selection when a probe atom jumps.

### 6.3 PAC Results

PAC measurements were made at various temperatures up to ~1200 K. PAC quadrupole perturbation functions for probe atoms on the $A$-sublattice exhibited no significant inhomogeneous broadening near ambient temperature, indicating a high degree of atomic order in the phases. Representative spectra measured at ~1120K for light (Pr) and heavy (Tm) lanthanide indides are compared in Fig. 6.2 for both $A$-rich and
B-rich boundary compositions [17]. QI signals having ~100-ns period are from probe atoms on the A-sublattices. Damping is visibly greater for A-richer In₃Pr and for B-richer In₃Tm.

Figure 6.2: PAC spectra for In₃Pr (left) and In₃Tm (right) for (A)-rich and (B)-rich compositions [17].

Principal axes of EFGs at adjacent A-sites are orthogonal, and the EFG reorients by 90º for probes jumping on the A-sublattice (see Fig. 6.1). This leads to a loss of coherence that was analyzed to determine mean jump frequency. PAC spectra were fitted with a quadrupole perturbation function $G_2(t)$ of the form:

$$G_2(t) = \exp(-wt)G_2^{static}(t),$$

which is a good approximation to the exact dynamically damped perturbation function in the slow fluctuation regime, which appears when the jump frequency is less than the quadrupole interaction frequency [12, 70]. For the particular jump model here, with
reorientations of the EFG tensor by 90° in each jump, the factor $w$ is the mean jump frequency (inverse of the mean residence time of the probe atom on a site of the $A$-sublattice). Fig. 6.3 shows PAC spectra for $^{111}\text{In/Cd}$ probe jumps in In-rich In$_3$La [12] for the three relaxation regimes: fast fluctuation ($w > \omega_1$) at 692 and 902 K, crossover ($w \sim \omega_1$) at 613 K and slow fluctuation ($w < \omega_1$) at 429 and 534 K [71].

Figure 6.3: PAC spectra [12] for $^{111}\text{In/Cd}$ probe jumps in In-rich In$_3$La showing three relaxation regimes: fast fluctuation ($w > \omega_1$) at 692 and 902 K, crossover ($w \sim \omega_1$) at 613 K and slow fluctuation ($w < \omega_1$) at 429 and 534 K.
Temperature dependence of the jump frequency is shown in Fig. 6.4 for $^{111}\text{In/Cd}$ jumping in In$_3$Pr (left) and In$_3$Tm (right) for In-rich and In-poor compositions fitted to the form:

$$w = w_0 \exp(-Q/k_B T)$$

(6.7)

where $w_0$ is a jump attempt frequency and $Q$ is the activation enthalpy for Cd probes to jump [17]. As can be seen, jump frequencies $w_A$ at the $A$-rich boundary are greater than jump frequencies $w_B$ at the $B$-rich boundary for In$_3$Pr whereas $w_A < w_B$ for In$_3$Tm. Measurements were made on opposing phase boundaries of various In$_3$R phases (see Table 6.1) and the jump frequency was found to be highly dependent on the composition of the sample. A reversed composition dependence was observed between the light and heavy rare earth indides, which strongly suggests the existence of different diffusion mechanisms.

![Figure 6.4: Arrhenius plots of fitted jump frequencies for In$_3$Pr (left) and In$_3$Tm (right) [17].](image-url)
Additional measurements were made at opposing phase boundary compositions for: \( \text{Sn}_3\text{La}, \text{Sn}_3\text{Ce}, \text{Sn}_3\text{Pr}, \text{Sn}_3\text{Nd}, \text{Sn}_3\text{Sm} \) and \( \text{Sn}_3\text{Gd} \) [18]. An earlier account of measurements on \( \text{Sn}_3\text{La} \) was given in ref. [65]. Fig. 6.5 shows a comparison of temperature dependences of jump frequencies for \( \text{In}_3\text{La} \) and \( \text{Sn}_3\text{La} \) at opposing phase boundary compositions. Jump frequencies were greater for the Sn-poor composition of \( \text{Sn}_3\text{La} \), in contrast to \( \text{In}_3\text{La} \).

![Figure 6.5](image)

**Figure 6.5:** Comparison of jump frequencies in In-rich and In-poor stannides and indides [18].

Table 6.1 lists fitted jump-frequency activation enthalpies and prefactors for aluminides, gallides, indides and stannides. For all stannides it was found that jump frequencies were greater for the Sn-poor composition of \( \text{Sn}_3R \) in contrast with \( \text{In}_3R \).
compounds. In addition, it is noteworthy that the jump frequencies in the indides differ by factors up to 10-100, but only by a factor of three in the stannides.
Table 6.1: Fitted values of activation enthalpies and jump attempt frequencies in various $L_1_2$ intermetallics for ($A$)-rich and ($B$)-rich compositions. The phase boundary is unknown if not listed.

<table>
<thead>
<tr>
<th>Phases</th>
<th>$Q$(eV)</th>
<th>$w_0$(THz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$_3$Dy ($B$)</td>
<td>1.04(9)</td>
<td>1.6(1.7)</td>
<td>[64]</td>
</tr>
<tr>
<td>Ga$_3$Er ($B$)</td>
<td>0.86(5)</td>
<td>1.7(1.3)</td>
<td>[64]</td>
</tr>
<tr>
<td>Ga$_3$Lu ($B$)</td>
<td>1.10(6)</td>
<td>3.5(2.5)</td>
<td>[64]</td>
</tr>
<tr>
<td>Al$_3$Er ($B$)</td>
<td>1.6(2)</td>
<td>106(208)</td>
<td>[64]</td>
</tr>
<tr>
<td>Al$_3$Tm</td>
<td>1.6(1)</td>
<td>100(+100,-50)</td>
<td>[72]</td>
</tr>
<tr>
<td>Al$_3$Lu</td>
<td>1.6(1)</td>
<td>100(+100,-50)</td>
<td>[72]</td>
</tr>
<tr>
<td>Al$_3$Yb</td>
<td>1.2(1)</td>
<td>27(+17,-11)</td>
<td>[72]</td>
</tr>
<tr>
<td>Sn$_3$La ($A$)</td>
<td>1.29(5)</td>
<td>14(9)</td>
<td>[65]</td>
</tr>
<tr>
<td>Sn$_3$La ($B$)</td>
<td>1.09(10)</td>
<td>3(4)</td>
<td>[65]</td>
</tr>
<tr>
<td>Sn$_3$Ce ($A$)</td>
<td>1.63(7)</td>
<td>69(51)</td>
<td>[18]</td>
</tr>
<tr>
<td>Sn$_3$Ce ($B$)</td>
<td>1.41(8)</td>
<td>26(245)</td>
<td>[18]</td>
</tr>
<tr>
<td>Sn$_3$Pr ($B$)</td>
<td>0.84(5)</td>
<td>0.11(6)</td>
<td>[18]</td>
</tr>
<tr>
<td>Sn$_3$Nd ($B$)</td>
<td>0.78(7)</td>
<td>0.05(4)</td>
<td>[18]</td>
</tr>
<tr>
<td>Sn$_3$Sm ($B$)</td>
<td>1.49(7)</td>
<td>134(99)</td>
<td>[18]</td>
</tr>
<tr>
<td>Sn$_3$Gd ($B$)</td>
<td>1.1(2)</td>
<td>2.8(5)</td>
<td>[18]</td>
</tr>
<tr>
<td>In$_3$La ($A$)</td>
<td>0.535(2)</td>
<td>1.02(0.05)</td>
<td>[65]</td>
</tr>
<tr>
<td>In$_3$La ($B$)</td>
<td>0.81(1)</td>
<td>1.4(0.2)</td>
<td>[65]</td>
</tr>
<tr>
<td>In$_3$Ce ($A$)</td>
<td>0.91(4)</td>
<td>1.7(+1.2,-0.7)</td>
<td>[65]</td>
</tr>
<tr>
<td>In$_3$Ce ($B$)</td>
<td>1.30(7)</td>
<td>11(+13,-6)</td>
<td>[65]</td>
</tr>
<tr>
<td>In$_3$Pr ($A$)</td>
<td>1.17(3)</td>
<td>3.5(1.3)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Pr ($B$)</td>
<td>1.75(9)</td>
<td>240(120)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Nd ($A$)</td>
<td>1.50(9)</td>
<td>27(25)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Nd ($B$)</td>
<td>1.4(1)</td>
<td>10(10)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Gd ($A$)</td>
<td>-2.3</td>
<td>-8000</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Gd ($B$)</td>
<td>1.36(1)</td>
<td>5.2(4.5)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Er</td>
<td>1.07(7)</td>
<td>0.62(+0.60,-0.31)</td>
<td>[65]</td>
</tr>
<tr>
<td>In$_3$Tm ($A$)</td>
<td>1.4(2)</td>
<td>5(8)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Tm ($B$)</td>
<td>1.2(1)</td>
<td>1.5(1.5)</td>
<td>[64]</td>
</tr>
<tr>
<td>In$_3$Y</td>
<td>1.43(5)</td>
<td>34(+26,-15)</td>
<td>[65]</td>
</tr>
<tr>
<td>In$_3$Lu ($A$)</td>
<td>2.0(3)</td>
<td>4(1)</td>
<td>[73]</td>
</tr>
<tr>
<td>In$_3$Lu ($B$)</td>
<td>1.17(4)</td>
<td>0.4(2)</td>
<td>[73]</td>
</tr>
</tbody>
</table>

As can be seen, activation enthalpies are all in the range 0.8-2.0 eV with prefactors of order 0.5-100 THz. The prefactors appear consistent with a vacancy diffusion mechanism, in which the magnitude is of the order of a vibrational frequency of an atom in a solid, serving as a jump attempt frequency.

For an $A_3B$ compound it makes a difference whether structural or thermally activated vacancies are on the $A$- or $B$-sublattices. This is illustrated in Fig. 6.6, showing two hypothetical diffusion mechanisms: a) $A$-vacancy sublattice diffusion and b) $B$-vacancy six-jump cycle (bent version shown). For the $A$-vacancy sublattice diffusion mechanism, an $A$-vacancy jumps on the $A$-sublattice, without creating lattice disorder. However, for the $B$-vacancy six-jump cycle, lattice disorder is created when the $B$-
vacancy jumps to near-neighbor sites. The defect combinations produced in the $B$-vacancy six jump cycle are (starting from a vacancy on the $B$-sublattice):

1$^{\text{st}}$ jump: $V_A + A_B$

2$^{\text{nd}}$ jump: $V_B + A_B + B_A$

3$^{\text{rd}}$ jump: $V_A + 2A_B + B_A$

4$^{\text{th}}$ jump: $V_B + A_B + B_A$

5$^{\text{th}}$ jump: $V_A + A_B$

6$^{\text{th}}$ jump: $V_B$

The sequence of six jumps eliminates disorder created by the first three jumps in the second three jumps. The $A$-vacancy mechanism is expected to lead to higher jump frequencies at the $A$-poor boundaries whereas the $B$-vacancy mechanism is expected to lead to higher jump frequencies at $B$-poor boundaries. Additionally, it is assumed that vacancy and antisite defects jump at a frequency comparable to that of Cd. Otherwise, some of the Cd probes in the vicinity of defects might jump at high frequency, while the probes that are far from defects will hardly jump at all. This would give a two signal spectra or significant inhomogeneous broadening of the spectra, which was not observed.
For binary compounds $A_3B$, it can be shown that the $A$-vacancy composition can only increase monotonically with increase in the $B$-composition [68]. Similarly, the concentration of $B$-vacancies increases as the composition becomes more $A$-rich. Consequently, if the greater jump frequency is observed at the $A$-rich boundary, then it is reasonable to conclude that the dominant diffusion mechanism must involve $B$-vacancies. Such is the situation for the light lanthanide indides ($R = \text{La, Ce, Pr, ...}$). Conversely, if the greater frequency is at the $B$-rich boundary, diffusion is likely to be dominated by $A$-vacancy diffusion mechanisms, such as for the heavy lanthanide indides ($R = \ldots, \text{Tm, Yb, Lu}$).
The change in mechanism between light and heavy lanthanide indides is likely to be caused by: (1) gradual changes in partial formation enthalpies of the four elementary point defects: $A$- and $B$-vacancies and $A_B$ and $B_A$ antisite atoms; and/or (2) gradual changes in migration enthalpies associated with jump barriers. The former cause was investigated in the present study.

6.4 DFT Results

To further understand the change in diffusion mechanism between light and heavy lanthanide indides, DFT was used to calculate formation enthalpies of defects in In$_3$La and In$_3$Lu since La is the lightest and Lu is the heaviest lanthanide. Calculations involved 2x2x2 supercells that took into account energy decreases associated with atomic relaxation around point defects. Additionally, EFGs were calculated for Cd impurities.

FP-(L)APW+lo was employed in order to calculate the structural and electronic properties of 2x2x2 In$_3$La and In$_3$Lu fully-relaxed supercells. Exchange and correlation effects were treated using GGA (PBE) [27]. For In$_3$La and In$_3$Lu, a $R_{MT}$ value of 2.5 bohr for both indium and rare earth atoms was used for all calculations. Inside the muffin-tin spheres, the wave functions, the electron charge densities and the potentials were expanded in terms of spherical harmonics up to angular momenta $l_{\text{max}}=10$. In the interstitial region they were expanded in plane waves with cutoff $R_{MT}K_{\text{MAX}} = 11.0$ for defect formation energy calculations and $R_{MT}K_{\text{MAX}} = 8.0$ for EFG calculations. For all calculations 63 $k$-points were used in the irreducible Brillouin zone for both In$_3$La and
In$_3$Lu. The iteration process was repeated until the calculated total energy converged to less than 0.1 mRy. Additionally, for EFG calculations, self-consistency was achieved by demanding the convergence of the integrated charge difference between the last two iterations to be better than $10^{-3}e$. Defect formation energies and site EFGs were calculated using optimized lattice parameters and relaxed atom positions.

Lattice parameters were optimized using conventional unit cells and are listed in Table 6.2. Optimized lattice parameters were respectively 3% and 1% larger than experiment [67] for In$_3$La and In$_3$Lu.

Table 6.2: Comparison of experimental and DFT calculated lattice parameters In$_3$La and In$_3$Lu.

<table>
<thead>
<tr>
<th></th>
<th>In$_3$La</th>
<th>In$_3$Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp. [67]</td>
<td>DFT</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.642</td>
<td>4.795</td>
</tr>
<tr>
<td>volume (Å$^3$)</td>
<td>100.03</td>
<td>110.25</td>
</tr>
</tbody>
</table>

The temperature dependences of the $V_{zz}$ for $^{111}$In/Cd probes in $B$-poor In$_3$La and In$_3$Lu compounds measured using PAC were fitted using the relation $V_{zz}(T) = V_{zz}(0)(1 - BT^{3/2})$. Fitted quadrupole interaction parameters and corresponding asymmetry parameters for $^{111}$In/Cd probes in In$_3$La and In$_3$Lu are given in Table 6.3.
Table 6.3: Experimental quadrupole interaction parameters for $^{111}$In/Cd probes in In-rich In$_3$La and In$_3$Lu. ($V_{zz}$ in units of $10^{21}$ V/m$^2$).

<table>
<thead>
<tr>
<th></th>
<th>$V_{zz}$ (0 K)</th>
<th>$B$ (K$^{3/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_3$La</td>
<td>3.60(1)</td>
<td>5.5(1) x 10$^{-6}$</td>
</tr>
<tr>
<td>In$_3$Lu</td>
<td>4.15(2)</td>
<td>5.3(1) x 10$^{-6}$</td>
</tr>
</tbody>
</table>

A comparison of calculated and measured (extrapolated to $T = 0$ K) EFGs at Cd sites in In$_3$La and In$_3$Lu is given in Table 6.4. Asymmetry parameters for Cd at either site were calculated to be small, $\eta < 0.02$ for both In$_3$La and In$_3$Lu. For In$_3$La, EFGs were calculated to be $V_{zz} < +0.02 \times 10^{21}$ V/m$^2$ for Cd$_{La}$ and $V_{zz} = +4.14 \times 10^{21}$ V/m$^2$ for Cd$_{In}$. Site EFGs in In$_3$Lu were calculated to be $V_{zz} < +0.02 \times 10^{21}$ V/m$^2$ for Cd$_{La}$ and $V_{zz} = +4.83 \times 10^{21}$ V/m$^2$ for Cd$_{In}$. Calculated EFG values for Cd$_{In}$ in In$_3$La and In$_3$Lu were respectively 0.54 and 0.58 x $10^{21}$ V/m$^2$ lower than measured values.

Table 6.4: Comparison of calculated and measured site $V_{zz}$ for Cd in In$_3$La and In$_3$Lu in units of $10^{21}$ V/m$^2$.

<table>
<thead>
<tr>
<th>Site</th>
<th>DFT</th>
<th>PAC</th>
<th>$V_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_3$La</td>
<td>La &lt;0.02</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In  4.14</td>
<td>3.60(1)</td>
<td></td>
</tr>
<tr>
<td>In$_3$Lu</td>
<td>Lu &lt;0.02</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In  4.83</td>
<td>4.15(2)</td>
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</tbody>
</table>
Listed in Table 6.5 are the calculated ground state energies for point defects in 2x2x2 supercells. $E_0$ is the total energy of defect free cell (32-atoms), $E(V_{\text{In}})$ and $E(V_{\text{R}})$ are the energies of cells (31-atoms) with vacancy defects and $E(R_{\text{In}})$ and $E(In_{\text{R}})$ are the energies of cells (32-atoms) containing antisite defects.

Table 6.5: Calculated ground state energies of point defects in In$_3$R and energies for bulk metals.

<table>
<thead>
<tr>
<th>Defect</th>
<th>In$_3$La</th>
<th>In$_3$Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>-418362.4260</td>
<td>-515697.8321</td>
</tr>
<tr>
<td>$E(V_{\text{In}})$</td>
<td>-406595.7143</td>
<td>-503931.1396</td>
</tr>
<tr>
<td>$E(V_{\text{R}})$</td>
<td>-401366.8619</td>
<td>-486535.4174</td>
</tr>
<tr>
<td>$E(R_{\text{In}})$</td>
<td>-423591.0870</td>
<td>-533093.5399</td>
</tr>
<tr>
<td>$E(In_{\text{R}})$</td>
<td>-413133.5149</td>
<td>-498302.0007</td>
</tr>
<tr>
<td>$E(\text{In})$ (Ry/atom)</td>
<td>-11766.6107</td>
<td></td>
</tr>
<tr>
<td>$E(\text{La})$ (Ry/atom)</td>
<td>-16995.3246</td>
<td></td>
</tr>
<tr>
<td>$E(\text{Lu})$ (Ry/atom)</td>
<td>-29162.3030</td>
<td></td>
</tr>
</tbody>
</table>

From the ground state energies of point defects, defect formation energies of elementary vacancy and antisite-atom defects, $V_{\text{In}}, V_{\text{R}}, In_{\text{R}}, R_{\text{In}}$, were obtained and are listed in Table 6.6. Vacancy defect formation energy $G(V_A)$ is defined as the energy needed to remove an $A$-atom from the $A_3B$ crystal to a reservoir, taken as bulk $A$. $G(V_A)$ is calculated as the energy difference between the total energies of the cell with ($E(V_A)$)
and without \((E_0)\) a vacancy plus the chemical potential of element \(A\) (\(E(A)\)). Antisite defect formation energy \(G(A_B)\) is defined as the energy needed to insert an \(A\)-atom, taken from a reservoir (bulk \(A\)), into the \(A_3B\) crystal after removing one \(B\)-atom to a reservoir (bulk \(B\)). \(G(A_B)\) is calculated as the difference between the total energies of the cell with and without the antisite defect plus the chemical potential of element \(B\) and the (negative) chemical potential of element \(A\). \(G(V_B)\) and \(G(B_A)\) have analogous definitions.

Chemical potentials of In, La and Lu were obtained for the corresponding most stable elemental structure of each \([74, 75]\): fct for In, dhcp for La and hcp for Lu. It is important to note that alternative reference states could have been energies of isolated gas atoms of each element. The cohesive energy of \(In_3R\), denoted as \(uc\), is defined as the difference in energy between the \(In_3R\) crystal \((E_0)\) and sum of the chemical potentials of the constituent atoms (\(E(In)/N\) and \(E(R)/N\)).

### Table 6.6: Calculated defect formation energies for \(In_3La\) and \(In_3Lu\) (in units of eV).
The cohesive energy of a unit cell is denoted as \(uc\). \(E(In)/N\) and \(E(R)/N\) are the total energies per atom of the bulk metals in their corresponding crystal structures.

<table>
<thead>
<tr>
<th>Definition</th>
<th>(In_3La)</th>
<th>(In_3Lu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell</td>
<td>(uc = E_0/8 - 3E(In)/N - E(R)/N)</td>
<td>-1.99</td>
</tr>
<tr>
<td>(A)-vacancy</td>
<td>(G(V_A) = E(V_{In}) + E(In)/N - E_0)</td>
<td>1.37</td>
</tr>
<tr>
<td>(B)-vacancy</td>
<td>(G(V_B) = E(V_R) + E(R)/N - E_0)</td>
<td>3.26</td>
</tr>
<tr>
<td>(B_A)-antisite</td>
<td>(G(B_A) = E(R_{In}) + E(In)/N - E(R)/N - E_0)</td>
<td>0.72</td>
</tr>
<tr>
<td>(A_B)-antisite</td>
<td>(G(A_B) = E(In_R) + E(R)/N - E(In)/N - E_0)</td>
<td>2.68</td>
</tr>
</tbody>
</table>
Energies of formation per defect of defect combinations in $\text{In}_3\text{La}$ and $\text{In}_3\text{Lu}$ are listed in Table 6.7. Formation energies of defect combinations, $G_{4V}$, $G_{2A}$ and $G_5$, are calculated as the sums of energies of the constituent defects plus, if a new unit cell is formed, the (negative) cohesive energy of a unit cell [68]. Formation energies of defect combinations are independent of reference states $E(\text{In})$ and $E(R)$.

<table>
<thead>
<tr>
<th>Definition</th>
<th>$\text{In}_3\text{La}$</th>
<th>$\text{In}_3\text{Lu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four-vacancy</td>
<td>$G_{4V} = (3G(V_A) + G(V_B) + uc)/4$</td>
<td>1.35</td>
</tr>
<tr>
<td>Antisite pair</td>
<td>$G_{2A} = (G(A_B) + G(B_A))/2$</td>
<td>1.70</td>
</tr>
<tr>
<td>Five-defect</td>
<td>$G_5 = (4G(V_A) + G(A_B) + uc)/5$</td>
<td>1.24</td>
</tr>
</tbody>
</table>

6.4 Calculated Defect Concentrations

Using the law of mass action, expressions of equilibrium constants for the formation reactions (Eqs. 6.1 - 6.3) in terms of powers of concentrations of the constituent elementary defects are

$$K_{4V} = [V_A]^3[V_B] = \exp\left(-\frac{G_{4V}}{k_BT}\right),$$

$$K_{2A} = \frac{[A_B][B_A]}{(1-[A_B]-[V_A])(1-[A_B]-[V_B])} = \exp\left(-\frac{G_{2A}}{k_BT}\right).$$

90
Concentrations of point defects in In$_3$La and In$_3$Lu were calculated as a function of composition and temperature by inserting Eqs. 6.8 – 6.10 into Eq. 6.4. Defect concentrations as a function of composition at 600 K are shown in Fig. 6.7 for In$_3$La (left) and In$_3$Lu (right).

As can be seen, deviations from stoichiometry in In$_3$La are accommodated by vacancies on the In-sublattice for La-rich ($x < 0$) and via In$_{La}$ antisite defects for In-rich ($x > 0$) compositions. Whereas La-vacancies and La$_{In}$ antisite defects play a negligible role throughout: their concentrations are so small that the corresponding curves virtually coincide with the $x$-axis in Fig. 6.7. Similarly for In$_3$Lu, deviations from stoichiometry are caused primarily by In-vacancies for Lu-rich and In$_{Lu}$ antisite defects for In-rich compositions. However, the concentrations [Lu$_{In}$] for Lu rich and concentrations [V$_{In}$] and [V$_{Lu}$] for In-rich are not negligible. At stoichiometry ($x = 0$), $A$-vacancy concentrations for In$_3$La and In$_3$Lu respectively are [V$_A$] = 0.011 and 0.027. $B$-vacancy concentrations for In$_3$La and In$_3$Lu respectively are [V$_B$] = 4.0 x 10$^{-6}$ and [V$_B$] = 0.002.
Figure 6.7: Calculated concentrations of four types of defects in In$_3$La (left) and In$_3$Lu (right) versus deviation from stoichiometry $x$.

To study the behavior of the constitutional point defects in In$_3$R, concentrations were also calculated as a function of temperature. Three compositions are shown: $A_{2.92}B_{1.08}$, $A_3B$ and $A_{3.08}B_{0.92}$ for In$_3$La in Fig. 6.8 and for In$_3$Lu in Fig. 6.9. For In$_{2.92}$La$_{1.08}$ (Fig. 6.8 a) the concentrations $[V_{La}]$, $[In_{La}]$ and $[La_{In}]$ increase significantly with increase in temperature but of $[V_{In}]$ remains virtually independent on temperature. As such, In-vacancy defects are constitutional defects resulting from the deviation in stoichiometry and the other three defects are thermal defects which are introduced by thermal activation. For In$_3$La (Fig. 6.8 b), all four defects increase with increasing temperature and are therefore thermal defects. In$_{La}$ antisite defects are constitutional defects in In$_{3.08}$La$_{0.92}$ (Fig. 6.8 c) as they are virtually independent on temperature and the other defects are thermal defects.
For In$_{2.92}$Lu$_{1.08}$ (Fig. 6.9 a) the concentrations $[V_{Lu}]$, $[In_{Lu}]$ increase significantly with increase in temperature, $[V_{In}]$ only slightly increases and $[Lu_{In}]$ remains virtually independent on temperature. In fact, $[Lu_{In}]$ slightly decreases with increasing temperature. As such, Lu$_{In}$ antisite defects are constitutional defects in Lu-rich phases and the other three are thermal defects. At stoichiometry, all four types of defects are thermal defects in In$_3$Lu as can be seen in Fig. 6.9 b. In the In-rich In$_{3.08}$Lu$_{0.92}$ phase (Fig. 6.9 c) In$_{Lu}$ antisite defects are constitutional defects and the other three are thermal defects.
Figure 6.9: Calculated concentrations of four types of defects versus temperature in In$_3$Lu for a) $B$-rich, b) stoichiometric and c) $A$-rich compositions.

A comparison of calculated defect concentrations for $A$-rich, stoichiometric, $B$-rich $A_3B$ compounds are given in Table 6.8. As can be seen, for both In$_3$La and In$_3$Lu, $A_B$ antisite defects dominate at the $A$-rich boundary and $V_A$ defects dominate stoichiometric and $B$-rich boundary in contrast to what was expected based on PAC measurements.
Table 6.8: Comparison of calculated defect concentrations for $A$-rich, stoichiometric and $B$-rich $\text{In}_3\text{La}$ and $\text{In}_3\text{Lu}$. Constitutional defect concentrations are indicated by superscript $\ast$.

<table>
<thead>
<tr>
<th></th>
<th>In$_3$La</th>
<th>In$_3$Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$-rich</td>
<td>$(x = 0.02)$</td>
<td>$[A_B] \ast &gt; [V_A] &gt; [V_B] &gt; [B_A]$</td>
</tr>
<tr>
<td></td>
<td>Stoich. $(x = 0.00)$</td>
<td>$[V_A] &gt; [A_B] &gt; [V_B] &gt; [B_A]$</td>
</tr>
<tr>
<td>$B$-rich</td>
<td>$(x = -0.02)$</td>
<td>$[V_A] \ast &gt; [B_A] &gt; [A_B] &gt; [V_B]$</td>
</tr>
</tbody>
</table>

### 6.5 Discussion

Diffusion is mediated by lattice vacancies in close-packed alloys of elements that have similar atomic radii such as for rare earth elements and indium [10]. In principle, either $A$- or $B$-sublattice vacancies, $V_A$ or $V_B$, may be involved. The vacancy type that predominates in diffusion of probe atoms was identified by the ratio $w_A/w_B$ measured with PAC. In the absence of interactions among point defects, it can be shown that, at a given temperature, the mole fraction of $V_A$ must increase monotonically as the content of element $A$ decreases, and similarly for $V_B$. Consequently, $[V_A]$ is greater at the $A$-poorer ($B$) and $[V_B]$ is greater at the $A$-richer ($A$) boundary compositions. From jump frequency measurements, it was concluded that diffusion in heavy (or light) lanthanide indides is dominated by mechanisms involving $V_A$ (or $V_B$). Accordingly, the diffusion mechanism for heavy lanthanide indides is most likely the $A$-vacancy sublattice mechanism and most
likely the B-vacancy six-jump cycle mechanism for light lanthanide indides. It is important to note that jump frequency observed using PAC is for an impurity $^{111}$Cd atom and not a host indium atom. Thus, jump frequencies of indium host atoms may conceivably be different. Nevertheless, conclusions about diffusion mechanisms based on differences in jump frequencies at boundary compositions remain valid for both host and impurity tracers.

Calculated concentrations of defects based on results of DFT calculations in In$_3$La and In$_3$Lu revealed that, for both of these compounds, $A_B$ antisite defects dominate at the $A$-rich boundary composition and $V_A$ defects dominate stoichiometric and $B$-rich boundary composition in contrast to what is expected if diffusion in heavy (or light) lanthanide indides is dominated by mechanisms involving $V_A$ (or $V_B$). This suggests that the change in mechanism between light and heavy lanthanide indides is not caused by gradual changes in partial formation enthalpies of the four elementary point defects but rather by gradual changes in migration enthalpies associated with jump barriers.
Bibliography


[73] This work.


Appendix

Table A1: Description and model numbers of PAC electronics.

<table>
<thead>
<tr>
<th>Model No. and description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMP</td>
</tr>
<tr>
<td>Ortec 575 amplifier</td>
</tr>
<tr>
<td>SCA</td>
</tr>
<tr>
<td>Ortec 551 timing single-channel analyzer</td>
</tr>
<tr>
<td>TAC</td>
</tr>
<tr>
<td>Ortec 567 time-to-amplitude converter</td>
</tr>
<tr>
<td>CFDD</td>
</tr>
<tr>
<td>Ortec 583 constant fraction differential discriminator</td>
</tr>
<tr>
<td>ADCAM</td>
</tr>
<tr>
<td>Ortec 918A analog-to-digital converter and memory</td>
</tr>
<tr>
<td>DDG</td>
</tr>
<tr>
<td>EG&amp;G PARC 9650 digital delay generator</td>
</tr>
<tr>
<td>Router</td>
</tr>
<tr>
<td>Energy logic and router tests for one and only one valid start/stop signal (home built TTL)</td>
</tr>
<tr>
<td>PM tube</td>
</tr>
<tr>
<td>Hamamatsu R2059 Quartz window photomultiplier tube</td>
</tr>
<tr>
<td>BaF$_2$ scintillators</td>
</tr>
<tr>
<td>cylindrical: 1.5&quot; diameter by 1&quot; long</td>
</tr>
<tr>
<td>Ortec 556 high voltage DC power supply</td>
</tr>
<tr>
<td>Ortec HVF-4 high voltage fanout</td>
</tr>
<tr>
<td>PC with old ISA data bus to connect to ADCAM</td>
</tr>
</tbody>
</table>

Table A2: Muffin-tin radii for all $A_3B$ systems in this work ($A =$ Al, In and $B =$ Ni, Ti, Zr, La, Lu).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$R_{MT}$ values in units of bohr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_3$Ni</td>
</tr>
<tr>
<td>$A$</td>
<td>2.14</td>
</tr>
<tr>
<td>$B$</td>
<td>2.41</td>
</tr>
</tbody>
</table>
Figure A1: $\text{Al}_3\text{Ni} \ (D_{020})$ energy versus $k$-points (left) and $R_{MT}K_{\text{MAX}}$ (right).

Figure A2: $\text{Al}_3\text{Ti} \ (D_{022})$ energy versus $k$-points (left) and $R_{MT}K_{\text{MAX}}$ (right).
Figure A3: \( \text{Al}_3\text{Zr} (D0_{23}) \) energy versus \( k \)-points (left) and \( R_{MT} K_{\text{MAX}} \) (right).

Figure A4: \( \text{In}_3\text{La} (L1_2) \) energy versus \( k \)-points (left) and \( R_{MT} K_{\text{MAX}} \) (right).
Figure A5: In$_3$Lu ($L1_2$) energy versus $k$-points (left) and $R_{MT}K_{MAX}$ (right).
Table A3: Results of $k$-point and $R_{MT K_{\text{max}}}$ convergence test for Al, In, La, Lu, Ni, Ti and Zr bulk metals results using 1x1x1 unit cells with experimental lattice constants (Å) (Note: the indium energy calculation was spin-polarized).

<table>
<thead>
<tr>
<th>metal</th>
<th>structure</th>
<th>$k$ - points</th>
<th>$R_{MT K_{\text{max}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>A1 (fcc)</td>
<td>$a = 4.0218$</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 145$</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>A6 (fct)</td>
<td>$a = 3.2522$</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 196$</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>A3' (dhcp)</td>
<td>$a = 3.7220$</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 144$</td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>A3 (hcp)</td>
<td>$a = 3.500$</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 165$</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>A1 (fcc)</td>
<td>$a = 3.520$</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>A3 (hcp)</td>
<td>$a = 2.9343$</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 150$</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>A3 (hcp)</td>
<td>$a = 3.232$</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 135$</td>
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</table>


Table A4: Measured and optimized lattice parameters (Å) for Al, In, La, Lu, Ni, Ti and Zr bulk metals.

<table>
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<tr>
<th></th>
<th>Al</th>
<th>Ni</th>
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<tbody>
<tr>
<td></td>
<td>Exp. [76]</td>
<td>Optimized</td>
</tr>
<tr>
<td>a</td>
<td>4.022</td>
<td>4.043</td>
</tr>
<tr>
<td>b</td>
<td>4.022</td>
<td>4.043</td>
</tr>
<tr>
<td>c</td>
<td>4.022</td>
<td>4.043</td>
</tr>
<tr>
<td>V</td>
<td>65.052</td>
<td>66.062</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>In (spin-polarized)</th>
<th>Ti</th>
<th>Zr</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Exp. [78]</td>
<td>Optimized</td>
</tr>
<tr>
<td>a</td>
<td>3.252</td>
<td>3.313</td>
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<tr>
<td>b</td>
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<td>3.313</td>
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<td>c</td>
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<td>5.039</td>
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<td>c/a</td>
<td>1.521</td>
<td>1.521</td>
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<tr>
<td>V</td>
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<table>
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<tr>
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<td>c/a</td>
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<tr>
<td>V</td>
<td>118.819</td>
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