

## Diffusion in Intermetallic Compounds Studied Using Nuclear Quadrupole Relaxation

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**Abstract.** The jump frequency of Cd tracer atoms was measured as a function of temperature in seven rare-earth tri-indide intermetallic compounds having the  $L1_2$ , or  $Cu_3Au$ , structure. The frequency, proportional to the diffusivity, was detected by relaxation of nuclear quadrupole interaction at Cd nuclei caused by reorientation of the electric field gradient in each diffusive jump. Measurements were made using perturbed angular correlation of gamma rays, sensitive to jump frequencies in the range 1-1000 MHz. Results are as follows. (1) Jump frequencies measured in  $LaIn_3$  and  $CeIn_3$  were observed to be 10-100 times greater at the more In-rich boundary composition than the less In-rich boundary composition, even though the phases appear as line compounds in phase diagrams. (2) Arrhenius plots of the jump frequency were fitted to activation enthalpies that increase from 0.535 to 1.80 eV across the series of phases  $LaIn_3$ ,  $CeIn_3$ ,  $PrIn_3$ , and  $NdIn_3$ .

### Introduction

Atom movement in solids is primarily studied in two different ways. The first involves measurement of the concentration profile of a tracer radionuclide diffused into a solid from the surface. The second involves measurement of an observable that is directly sensitive to the individual diffusive jumps. It has recently been shown that the electric field gradient (EFG) at the nucleus of a tracer atom can act as such an observable when the EFG reorients in each jump [1]. This was demonstrated in experiments using the method of perturbed angular correlation of gamma rays (PAC) for  $^{111}Cd$  tracer atoms jumping on the In-sublattice in  $In_3La$ , which has the  $L1_2$ , or  $Cu_3Au$ , structure [1]. To investigate the systematics of diffusion in the rare earth tri-indide series, measurements are reported in this paper on  $CeIn_3$ ,  $PrIn_3$ ,  $NdIn_3$ ,  $GdIn_3$ ,  $YIn_3$  and  $ErIn_3$ .

The jump frequency  $w$  is defined here as the inverse of the mean residence time of the tracer atom on a site. For diffusion on sublattices in cubic crystal structures, including the In-sublattice in these tri-indides,  $w$  is related to the diffusivity  $D$  via the relation [2]

$$D = \frac{1}{6} fw\ell^2, \quad (1)$$

in which  $f$  is the correlation coefficient of diffusion and  $\ell$  is the jump distance. For a vacancy mediated diffusion mechanism, the jump frequency would be interpreted in the usual way as [2]

$$w = z[V]w_2, \quad (2)$$

in which  $w_2$  is the frequency of exchange of the tracer with a neighboring vacancy,  $z$  is the number of neighboring sites on the diffusion sublattice (here,  $z=8$ ), and  $[V]$  is the mole fraction of vacancies on the diffusion sublattice.

The PAC technique involves measurement of the angular and time correlation of successive emissions of gamma rays from a probe nuclide for which the intermediate state is long-lived.

Algebraic combination of delayed coincidence spectra leads to a time-dependent perturbation function  $G_2(t)$ . In the present experiments,  $^{111}\text{Cd}$  probe atoms act as tracers on the In sublattice. The sites have tetragonal point symmetry and the static perturbation function has the form  $G_2^{static}(t) = \frac{1}{5} + \frac{13}{35} \cos(6\omega_Q t) + \frac{10}{35} \cos(12\omega_Q t) + \frac{5}{35} \cos(18\omega_Q t)$ , in which  $\omega_Q$  is the quadrupole interaction frequency. Reorientation of the EFG during the lifetime of the intermediate state (120 ns) leads to decoherence of the nuclear precessions. Assuming that tracers jump to near neighbor sites on the In sublattice, it can be readily seen that the axis of the EFG tensor reorients from one  $\langle 100 \rangle$  cube direction to a perpendicular cube direction in each jump. The dynamic perturbation function has been worked out exactly for this particular dynamic relaxation model for all ratios  $w/\omega_Q$  and has been used below to fit spectra measured in this study (see ref. [1] for details). The qualitative effect of nuclear relaxation on the perturbation function in the slow fluctuation regime ( $w < \omega_Q$ ) is described by the approximate perturbation function [3]

$$G_2(t) \cong \exp(-\lambda t) G_2^{static}(t), \quad (3)$$

in which the relaxation frequency  $\lambda$  can be shown to be equal to the jump frequency  $w$ :  $\lambda = w$  [1]. In the fast fluctuation regime ( $w > \omega_Q$ ), the approximate function from Ref. [3] is

$$G_2(t) \cong \exp(-200\omega_Q^2 t / 3w), \quad (4)$$

when rewritten in terms of the jump frequency.

## Experiments and Results

**Sample preparation.** Samples containing  $\text{In}_3\text{R}$  phases (R= La, Ce, Pr, Nd, Gd, Er, Y) were prepared by arc melting metal foils ( $\geq 99.9\%$  pure) with carrier-free  $^{111}\text{In}$  activity under argon. Quadrupole frequencies agreed excellently with those measured previously and attributed to  $^{111}\text{Cd}$  on the In-sublattice in the  $\text{L1}_2$  structure [4]. No other quadrupole interaction signals were observed that could be associated with point defects such as vacancies next to the tracers. While all phases appear as line compounds in binary phase diagrams [5], of necessity they must have finite field widths. To determine how the jump frequency varies as a function of composition, samples of  $\text{LaIn}_3$  and  $\text{CeIn}_3$  were prepared having excesses or deficits of In relative to the stoichiometric composition. Spectra from these samples exhibited small site fractions of quadrupole interaction from neighboring phases, and therefore can be assumed to have compositions at the more In-rich or less In-rich phase boundaries, respectively, designated as A and B below. Single samples were prepared with nominally stoichiometric compositions for the other five phases.

**PAC Measurements.** Measurements were made using a four-detector spectrometer. For further details about methods and the measurement oven, see Refs. [1,6]. Fig. 1 compares spectra of  $\text{LaIn}_3(\text{A})$ ,  $\text{LaIn}_3(\text{B})$ ,  $\text{CeIn}_3(\text{A})$  and  $\text{PrIn}_3$  measured at the same temperature of 902 K. The figure illustrates the effect of relaxation, with jump frequencies increasing as one goes from bottom to top in the figure. Spectra for  $\text{PrIn}_3$  and  $\text{CeIn}_3(\text{A})$  exhibit exponential damping of the static perturbation function, as in Eq. 3. Spectra for  $\text{LaIn}_3(\text{B})$  and  $\text{LaIn}_3(\text{A})$  are in the fast fluctuation regime. While the observed relaxation is smaller for  $\text{LaIn}_3(\text{A})$  than for  $\text{LaIn}_3(\text{B})$ , the jump frequency is in fact greater, as can be seen from Eq. 4. This is due to increased motional averaging of the EFG over the three EFG orientations for  $\text{LaIn}_3(\text{A})$ . With further increase in jump frequency, the EFG will approach the average over all orientations, or zero, so that  $G_2(t) \cong 1$ . Finally, all tracers can be seen to be participating homogeneously in the diffusional process.

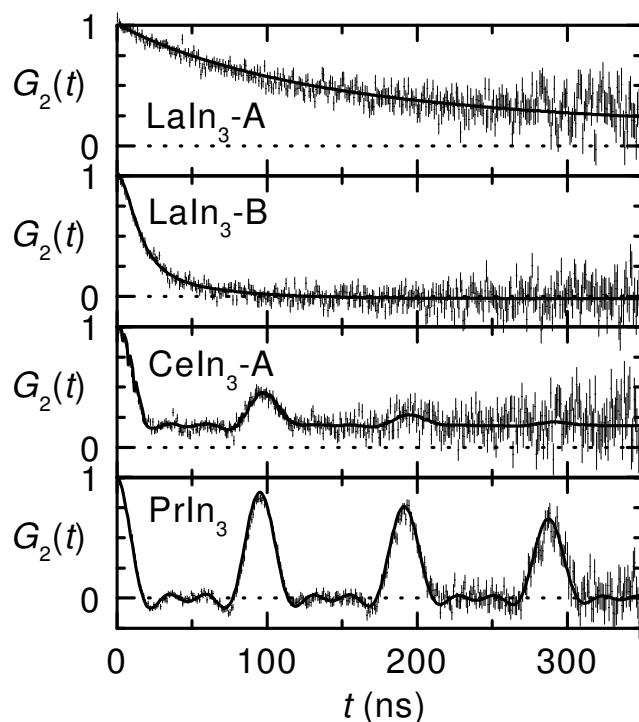


Fig. 1. PAC perturbation functions for  $^{111}\text{Cd}$  tracer atoms in  $\text{LaIn}_3$  (A),  $\text{LaIn}_3$  (B),  $\text{CeIn}_3$  (A) and  $\text{PrIn}_3$ , all measured at 902 K. Solid curves show results of fits to dynamic perturbation functions from which tracer jump frequencies were obtained. Approximate frequencies going from bottom to top are  $w = 3, 15, 80$  and  $100$  MHz.

**Arrhenius Plots.** Fig. 2 shows an Arrhenius plot of jump frequencies obtained from fitting the spectra (Gd and Ce(B) data sets are not shown for clarity). All nine data sets exhibited linear behavior and were fitted with expressions of the form  $w = w_0 \exp(-Q/k_bT)$  to obtain the jump frequency activation enthalpy  $Q$  and prefactor  $w_0$ . The composition dependence of the jump frequencies is illustrated in Fig. 3 by an Arrhenius plot of jump frequencies for phase boundary compositions of  $\text{LaIn}_3$  and  $\text{CeIn}_3$  that are more In-rich (A) and less In-rich (B). Based on the In-La and In-Ce phase diagrams and on lack of observable inhomogeneous broadening in measurements at low temperature where relaxation is negligible, it is believed that In compositions at the more In-rich boundaries (A) are of the order of 0.1 at.% In above the stoichiometric composition of 75.0 at.%In and that compositions of the less In-rich samples (B) are very close to the stoichiometric composition (cf. ref. [1]). Fitted activation enthalpies and frequency prefactors are given in Table 1. As can be seen, the activation enthalpies are extraordinarily low.

Table 1. Activation enthalpies and jump frequency prefactors for Cd tracers jumping on the In sublattice in  $\text{In}_3\text{R}$ .

R	$Q$ (eV)	$w_0$ (THz)
La (A)	0.535(2)	$1.02^{+0.05}_{-0.05}$
La (B)	0.81(1)	$1.4^{+0.2}_{-0.2}$
Ce (A)	0.91(4)	$1.7^{+1.2}_{-0.7}$
Ce (B)	1.30(7)	$11^{+13.}_{-6.}$
Pr	1.11(3)	$3.6^{+1.5}_{-1.1}$
Nd	1.80(5)	$450^{+290}_{-180}$
Gd	$\sim 1.2$	$\sim 3$
Er	1.07(7)	$0.62^{+0.60}_{-0.31}$
Y	1.43(5)	$34^{+26}_{-15}$

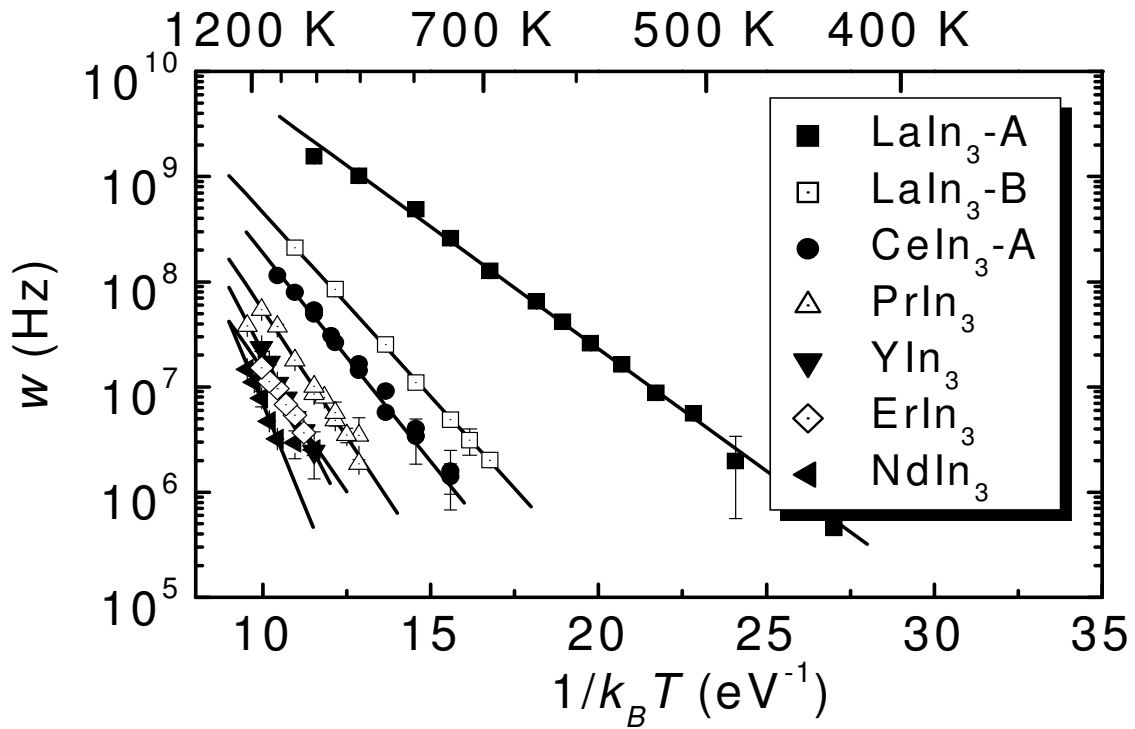


Fig. 2. Jump frequencies of  $^{111}\text{Cd}$  tracer atoms on the In sublattice. A and B indicate more In-rich and less In-rich phase boundary compositions.

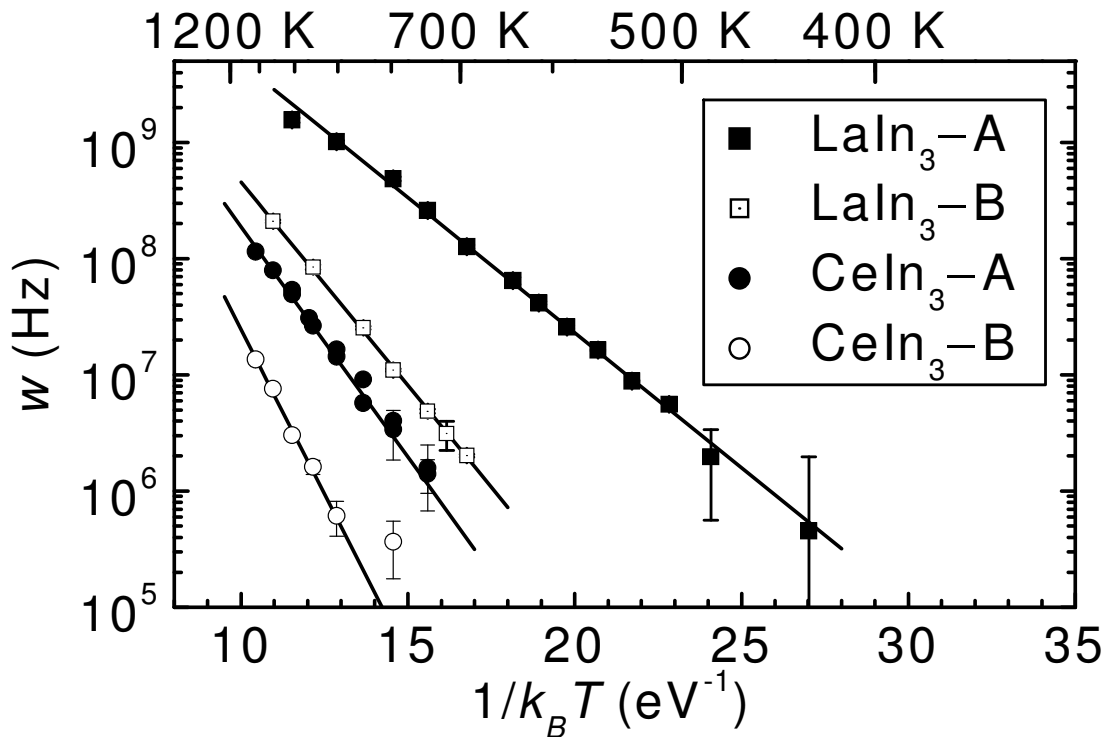


Fig. 3. Jump frequencies of  $^{111}\text{Cd}$  tracer atoms on the In sublattice. A and B indicate more In-rich and less In-rich phase boundary compositions.

## Discussion

**Trends Across the Rare Earth Phases.** Activation enthalpies in Table 1 appear to be correlated with lattice parameters, which decrease across the series of phases due to lanthanide contraction, and are plotted versus lattice parameters [4] in Fig. 4. Activation enthalpies for  $\text{LaIn}_3(\text{A})$ ,  $\text{CeIn}_3(\text{A})$  and  $\text{PrIn}_3$  fall on the dashed line and enthalpies for  $\text{LaIn}_3(\text{B})$ ,  $\text{CeIn}_3(\text{B})$  and  $\text{NdIn}_3$  fall on the solid line. The figure suggests that the  $\text{PrIn}_3$  and  $\text{NdIn}_3$  samples (compositions of which had not been measured precisely) had compositions at the more In-rich and less In-rich phase boundaries, respectively. Data for the remaining phases do not fall close to either line. Thus, activation enthalpies for early rare earth indides appear to increase with lattice parameter, as is natural to expect since the more open lattices should have lower barriers to migration on the In sublattice. Measurements on less In-rich  $\text{PrIn}_3$  and more In-rich  $\text{NdIn}_3$  could test this apparent systematic.

**Diffusion Mechanisms.** The most obvious mechanism to consider is diffusion of Cd tracers by exchange with vacancies on the In sublattice. From Fig. 3, it can be seen that jump frequencies are a factor of 10-100 times greater at the more In-rich phase boundary composition. However, the mole fraction of vacancies on the In sublattice can only decrease as the composition of In increases (see, e.g., Ref. [7].) Therefore, observation of greater jump frequencies at the more In-rich boundary compositions of  $\text{LaIn}_3$  and  $\text{CeIn}_3$  rules out this simple mechanism [1]. Other mechanisms compatible with the observed composition dependence include correlated motion of bound R and In vacancies, conversion of an R vacancy into a bound In antisite atom and In vacancy, and a six-jump cycle, described in more detail in Ref. [1]. Information is needed about vacancy and antisite defect formation energies in these phases to shed more light on the operative diffusion mechanisms.

**Magnitudes of the Activation Enthalpies and Prefactors.** Jump frequencies of Cd tracers are unusually large, especially for  $\text{LaIn}_3$  and  $\text{CeIn}_3$ . Converting jump frequencies to diffusivities using Eq. 1 while assuming a correlation factor of the order of unity leads to a very high value for  $\text{LaIn}_3(\text{A})$  at the melting temperature,  $\sim 10^{-10} \text{ m}^2/\text{s}$ , amongst the highest values for any solid. Frequency prefactors in Table 1 have a geometric average of  $5 \times 10^{12} \text{ Hz}$ . This appears to be a reasonable value for some kind of diffusion mechanism involving vacancies. Using Eq. 2, such a prefactor is consistent with  $z=8$  times a jump attempt frequency for exchange (a Debye frequency  $\sim 10^{14} \text{ Hz}$ ) times a vacancy mole fraction extrapolated to infinite temperature of  $10^{-1}$ .

**Features of the Nuclear Quadrupole Relaxation Method.** (1) Measurable jump frequencies are limited by the lifetime of the intermediate nuclear state and quadrupole interaction frequency, giving an accessible range of 1-1000 MHz for  $^{111}\text{Cd}$  PAC. This translates to diffusivities between  $10^{-14}$  and  $10^{-11} \text{ m}^2/\text{s}$  when one inserts  $f \cong 1$  in Eq. 1. (2) Measurements are restricted to a small number of PAC nuclides having favorable nuclear characteristics. (3) Measurements are restricted to jumps of tracers between sites having different orientations (or magnitudes) of EFGs. This rules out measurements for sublattices for which the EFG does not reorient in a jump (e.g., in  $\text{L1}_0$  phases). (4) The technique is well suited for the study of diffusion in slightly two-phase systems, as demonstrated in the present study by measurement of jump frequencies for boundary compositions of line compounds. (5) Measurements are undisturbed by short circuit diffusion paths as long as the number of tracer sites in the paths is much less than the number of volume sites, as is usually true.

**Future Prospects.** (1) Eq. 1 can be rewritten  $f = (6/\ell^2)(D/w)$ , from which it can be seen that the correlation factor can be obtained from complementary measurements of  $D$  and  $w$  made using the same tracer. Experimental measurements of  $f$  and its temperature dependence will help to elucidate diffusion mechanisms. (2) Crystal structures suitable for study besides  $\text{L1}_2$  include B20 (e.g., FeSi) and A13 (e.g.,  $\beta$ -Mn [8] and gamma brasses). Unique information may come from measurements of jump frequencies of a tracer that occupies inequivalent sublattices and has different quadrupole interactions. Differences or similarities between jump frequencies and activation enthalpies measured separately for each ensemble of tracers may shed light on whether or not tracer atoms diffuse in isolation on each sublattice or jump rapidly between them.

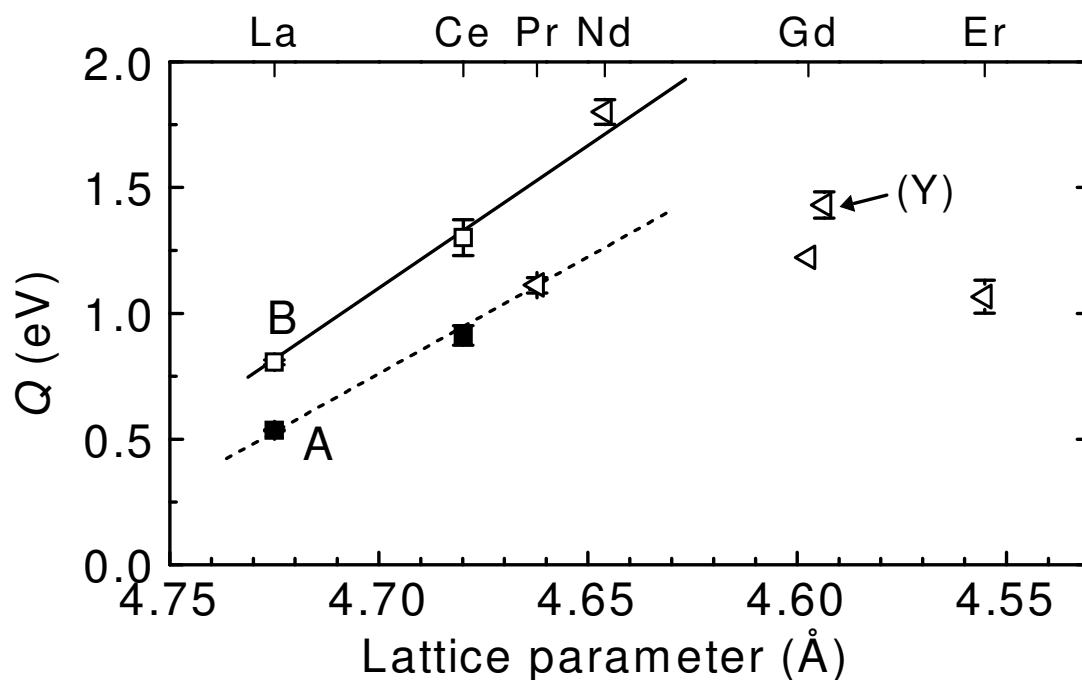


Fig. 4. Jump frequency activation enthalpy as a function of lattice parameter for  $\text{In}_3\text{R}$  phases ( $\text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Y}$  and  $\text{Er}$ ). Note the reversed lattice parameter scale. For La and Ce, filled and open symbols correspond to the more In-rich (A) and the less In-rich (B) phase boundary compositions.

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