

# Atom Movement in In<sub>3</sub>La Studied via Nuclear Quadrupole Relaxation

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Jump frequencies of Cd tracer atoms in In<sub>3</sub>La were measured via nuclear quadrupole relaxation caused by stochastic reorientation of the electric field gradient using the method of perturbed angular correlation of gamma rays. Activation enthalpies of 0.53(1) and 0.81(1) eV were found at the two phase boundaries, which differ in composition by only about 0.1 at. %. The jump frequency was found to be higher at the more In-rich phase boundary, ruling out a simple In-vacancy diffusion mechanism. Possible diffusion mechanisms and general applicability of the method are discussed.

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Atom movement in solids is conventionally studied by profiling the depth distribution of tracer atoms diffused into a sample [1]. An alternative approach is to measure in real time an observable that is sensitive to the discrete atomic jumps [2]. One such observable is the electric field gradient (EFG) detected at the nucleus of a jumping atom. When the geometry of the diffusion lattice is such that the EFG reorients in a jump, the quadrupole interactions of the ensemble of tracer nuclei will lose coherence over time. This is illustrated in the present study by quadrupole interactions of cadmium tracer atoms jumping on the indium sublattice in In<sub>3</sub>La, which has the Cu<sub>3</sub>Au, or L1<sub>2</sub>, structure (Fig. 1). Principal axes of EFGs at adjacent In sites are orthogonal, and the EFG reorients by 90° in each jump. The resulting loss of coherence was analyzed to determine the mean jump frequency as a function of temperature and composition.

Measurements were made by the method of perturbed angular correlation (PAC) of gamma rays [3] using radioactive <sup>111</sup>In probe atoms. <sup>111</sup>In decays with a half-life of 2.8 days through the 84 ns, spin-5/2, 247 keV level of <sup>111</sup>Cd via emission of two gamma rays. When an EFG is present at the Cd nucleus, the system is perturbed and populations of the magnetic substates of the 247 keV level evolve over the lifetime of the level. As a result, the angular correlation between the first and second gamma rays is time dependent and characterized by a perturbation function  $G_2(t)$ .

The crystal structure of In<sub>3</sub>La has a face centered cubic arrangement with La atoms at corners and In atoms at face centers of the conventional unit cell. The In site has tetragonal symmetry, so that the EFG is axially symmetric and the static perturbation function has the form  $G_2^{\text{static}}(t) = \frac{1}{35}[7 + 13 \cos(6\omega_Q t) + 10 \cos(12\omega_Q t) + 5 \cos(18\omega_Q t)]$  at low temperature. Here,  $t$  is the lifetime of the intermediate state and  $\omega_Q = \frac{\pi}{20}|eQV_{zz}|/h$  is the quadrupole interaction frequency, defined in terms of the quadrupole moment  $Q$  of the 247 keV level and the EFG  $V_{zz}$  at the nuclear site. Loss of coherence occurs when Cd tracer atoms jump during their lifetimes. When the jump frequency  $w$  of the tracer is low ( $w \ll \omega_Q$ ), reorientation

of the EFG attenuates, or damps out, the perturbation function. The dynamic perturbation function in this “slow fluctuation” regime can be expressed approximately in terms of the static function as  $G_2(t) \approx \exp(-\lambda t)G_2^{\text{static}}(t)$ , in which the relaxation frequency  $\lambda$  is proportional to  $w$  [4]. For the fast fluctuation regime ( $w \gg \omega_Q$ ), the perturbation function decays exponentially, in good approximation, as  $G_2(t) \approx \exp[-(100\omega_Q^2/3w)t]$  [4]. The present measurements span the slow and fast fluctuation regimes and include the intermediate regime ( $w \approx \omega_Q$ ) for which a satisfactory analytic approximation for  $G_2(t)$  does not exist. To obtain  $w$  and  $\omega_Q$  from measurements in all fluctuation regimes, we fitted experimental perturbation functions with numerical calculations of exact functions using the method of Winkler and Gerda [5] with improvements by Evenson *et al.* [6]. For  $w \geq \omega_Q$ ,  $w$  and  $\omega_Q$  are highly correlated and it is not possible to fit them independently; in this case we fitted  $w$  after fixing  $\omega_Q$  to values extrapolated from lower temperatures.

Samples of In<sub>3</sub>La were prepared by arc melting high purity metal foils with <sup>111</sup>In under argon. Typical samples had 30-mg masses and 10<sup>-8</sup> mole fractions of <sup>111</sup>In. The quadrupole interaction is axially symmetric with frequency  $\omega_Q = 11.34(1)$  Mrad/s at room temperature, the same as observed by Schwartz and Shirley [7], and is

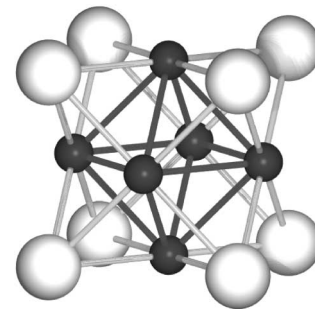


FIG. 1. Crystal structure of In<sub>3</sub>La, with In atoms at centers of cube faces. Principal axes of EFGs at In sites are normal to the cube faces. Near-neighbor jump vectors between In sites are shown by dark segments.

attributed to the lattice EFG. We used a conventional four-counter PAC spectrometer and methods of data analysis described elsewhere [8]. Measurements were made at temperatures up to 800 °C in vacuum under a pressure of about  $10^{-5}$  Pa. No evidence of point defects or phase disorder was observed in the measurements [9]. Inhomogeneous broadening was very small in spectra measured at room temperature, at which temperature atomic motion produces no detectable relaxation. Thus, all indications are that samples remained highly ordered and that concentrations of point defects were too small to detect.

An essential finding of the present measurements is that the jump frequency was found to depend strongly on composition, expressed below in terms of the deviation from stoichiometry  $x$  in the formula  $\text{In}_{3+4x}\text{La}_{1-4x}$ . While  $\text{In}_3\text{La}$  appears as a line compound in the In-La phase diagram [10], the phase field must have a finite, though possibly very narrow, width. From the small and large differences between melting temperatures of  $\text{In}_3\text{La}$  (1138 °C) and adjacent phases  $\text{In}_2\text{La}$  (1152 °C) and In metal (155 °C), one can conclude that the more In-rich phase boundary composition, designated  $x_1$ , is indeed In rich ( $x_1 > 0$ ) and that the less In-rich boundary composition,  $x_2$ , is very close to the stoichiometric composition ( $x_2 \approx 0$ ). To explore the composition dependence of the jump frequency in  $\text{In}_3\text{La}$ , In-La samples were made having average compositions close to 23 and 26 at.% La. Spectra for these samples exhibited small site fractions ( $\sim 5\%$ – $15\%$ ) of PAC signals of the neighboring phases (either In or  $\text{In}_2\text{La}$ ) in addition to the  $\text{In}_3\text{La}$  signal. Thus, these two-phase samples contained  $\text{In}_{3+4x}\text{La}_{1-4x}$  with  $x = x_1$  or  $x = x_2$ . We estimate that any defect concentration could be no larger than about 0.5 at.% based on lack of observation in any sample of (i) significant inhomogeneous broadening due to distant point defects and (ii) signals due to nearby structural point defects having site fractions greater than an observational threshold of about 4%. Consequently,  $x_1 \lesssim 0.001$  and  $x_2$  must be much smaller in magnitude.

Typical spectra for the In-rich phase boundary composition ( $x = x_1$ ) are shown in Fig. 2 for temperatures that span the slow and fast fluctuation regimes. At low temperature (156 °C, bottom panel), the spectrum exhibits essentially the static quadrupole perturbation function. Significant relaxation is observed at 261 °C that is attributed to jumping of Cd tracer atoms in the slow fluctuation regime. Maximum relaxation is observed at 340 °C, at and above which the perturbation function no longer obviously exhibits the periodic quadrupole interaction frequency  $\omega_Q$ . In the fast fluctuation regime at high temperatures (419 and 629 °C), the relaxation is observed to decrease with increasing temperature due to motional averaging. Spectra were fitted as described above, and fitted perturbation functions can be seen in Fig. 2 to be in excellent agreement with the data. Also, it is important

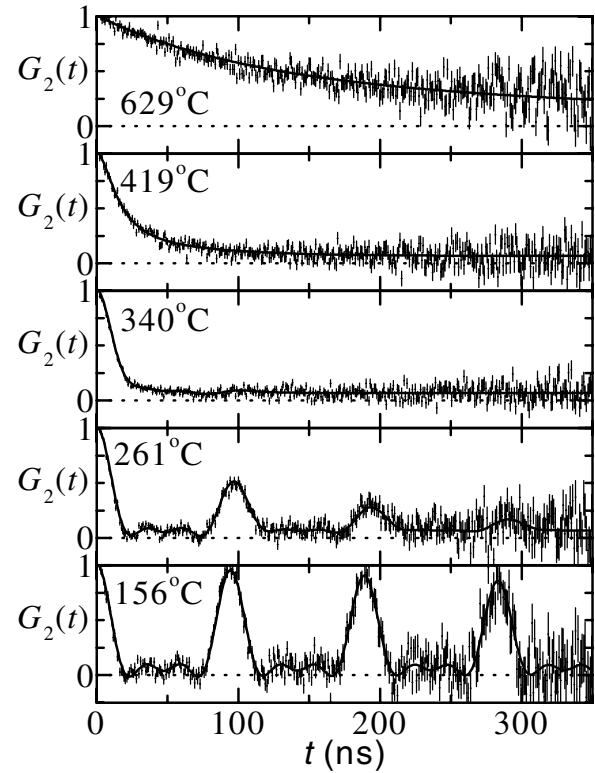


FIG. 2. Perturbation functions of  $^{111}\text{Cd}$  tracer atoms in  $\text{In}_3\text{La}$  at the indicated temperatures.

to note that the observed relaxation is homogeneous over all tracer atoms; that is, one does not observe subsets of tracer atoms with different relaxation rates.

Jump frequencies obtained from the fits are plotted in Fig. 3 versus reciprocal temperature. Data for two samples corresponding to phase boundary composition  $x_1$  are shown by squares and crosses. Data for a third

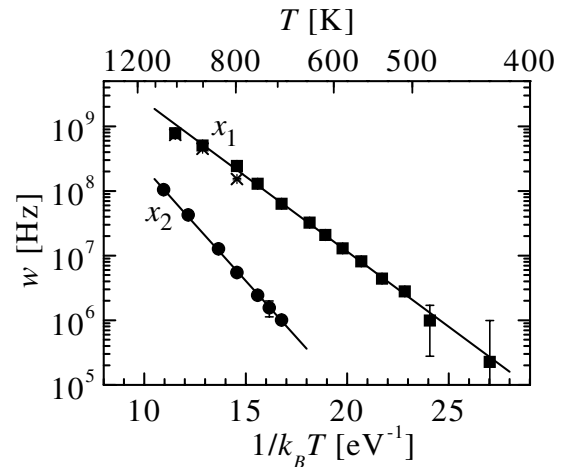


FIG. 3. Temperature dependence of the frequency of reorientation of the electric field gradient at the nuclei of Cd tracer atoms caused by jumps on the In sublattice in  $\text{In}_3\text{La}$ . The lines indicate fits of data for the two different compositions, with symbols and labels defined in the text.

sample having phase boundary composition  $x_2$  are shown by circles. Jump frequencies at  $x_1$  are greater by a factor of 10–100 than at  $x_2$  even though the boundary compositions differ by no more than about 0.1 at. %. Jump frequencies for compositions  $x_1$  and  $x_2$  were fitted with thermally activated expressions of the form  $w = w_0 \exp(-Q/k_B T)$ . Resulting fits are shown by straight lines in the figure, with  $Q_1 = 0.53(1)$  eV and  $Q_2 = 0.81(1)$  eV and corresponding prefactors  $w_{01} = 5.1(7) \times 10^{11}$  Hz and  $w_{02} = 7(1) \times 10^{11}$  Hz.

The jump frequency has to be interpreted in the context of a diffusion mechanism. We consider first the most elementary possible mechanism: diffusion by random jumping of In vacancies to near neighbor sites on the In sublattice. For this mechanism, the jump frequency  $w$  of a tracer atom is given by

$$w = z[V_{\text{In}}]w_2, \quad (1)$$

in which  $z$  is the number of near neighbor In sites ( $z = 8$ ),  $w_2$  is the frequency of exchange between a tracer atom and vacancy next to it, and  $[V_{\text{In}}]$  is the fractional concentration of vacancies on the In sublattice [1]. The corresponding diffusivity of the tracer on the In sublattice in  $\text{In}_3\text{La}$  is  $D = \frac{2}{3}fa^2[V_{\text{In}}]w_2$  [11], in which the factor  $2/3$  arises from the geometry of the jump vectors on the In sublattice,  $f$  is the correlation coefficient for diffusion, and  $a$  is the lattice parameter (0.474 for  $\text{In}_3\text{La}$  [7]).  $D$  and  $w$  thus can be seen to be proportional via the relation

$$D = \frac{1}{12}fa^2w. \quad (2)$$

For this diffusion mechanism, the activation enthalpy of the jump frequency is given by the sum of an effective enthalpy of formation of In vacancies and a vacancy migration enthalpy  $H_M^V$  [1], assuming as usual that the exchange frequency is thermally activated according to  $w_2 = w_{20} \exp(-H_M^V/k_B T)$ . For self-diffusion, the correlation coefficient is  $f = 0.689$  [11], whereas for impurity diffusion it is generally a function of temperature [1,11]. To make a qualitative comparison between jump frequency and diffusivity measurements, one can insert the correlation coefficient for self-diffusion into Eq. (2), in which case the jump-frequency activation enthalpy  $Q$  is identical to the activation enthalpy for diffusion and the prefactor of the diffusivity is  $\frac{1}{12}fa^2w_0$ . The value  $Q_1 = 0.53$  eV is unusually low when compared with activation enthalpies for diffusion in intermetallic compounds [12,13]. Also, the jump frequencies are unusually high at low temperature, with data for  $x = x_1$  extrapolating to a jump frequency of 400 Hz for Cd impurities at room temperature.

The composition dependence of the jump frequency gives insight into the diffusion mechanism. It can be shown from the thermodynamics of defects in  $L1_2$  compounds (e.g., see Ref. [14]) that  $[V_{\text{In}}]$  decreases and  $[V_{\text{La}}]$  increases monotonically with increasing  $x$ . For the In-

sublattice vacancy diffusion mechanism described above, the jump frequency at a given temperature is proportional to the concentration of In vacancies [see Eq. (1)]. Thus, this mechanism would lead to a *lower* Cd jump frequency as  $x$  increases, which is contrary to the results shown in Fig. 3, ruling out this diffusion mechanism. Likewise, the ring exchange mechanism [15] does not obviously have a strong composition dependence, although it could explain the absence of an observed defect signal since the mechanism does not require a defect.

Three diffusion mechanisms are consistent with the observed composition dependence: a La-vacancy six-jump cycle [16], a divacancy mechanism [17], and a vacancy conversion mechanism. In the six-jump cycle, a La vacancy makes a sequence of six near neighbor jumps on the In and La sublattices, resulting in the exchange of two atoms on the In sublattice and the exchange between the vacancy and a La atom on the La sublattice. In the divacancy mechanism, bound, near neighbor La- and In-vacancy pairs make correlated jumps on their respective sublattices. In the vacancy conversion mechanism,  $V_{\text{La}}$  converts into  $V_{\text{In}}$  via the reaction  $V_{\text{La}} + \text{In}_{\text{In}} \rightarrow V_{\text{In}}:\text{In}_{\text{La}}$  to form bound  $V_{\text{In}}:\text{In}_{\text{La}}$  pairs. The  $V_{\text{In}}$  thus formed is assumed to jump freely among the 12 neighbor sites of the associated  $\text{In}_{\text{La}}$  defect. Periodic reconstitution of the original  $V_{\text{La}}$  defect allows it to jump on its own sublattice. Homogeneity of the PAC perturbation function demonstrates that jump frequencies of  $V_{\text{La}}$  and  $V_{\text{In}}$  are comparable. Otherwise, there would be isolated motion of  $V_{\text{In}}$  defects around immobile defects on La sites, leading to a superposition of signals for tracer atoms jumping rapidly or not at all, contrary to observation.

For each of the three mechanisms, the jump frequency increases monotonically with  $[V_{\text{La}}]$ , which itself increases monotonically with  $x$ . The observed differences in activation enthalpies and relative values of  $x$  at the boundary compositions lead us to believe that  $V_{\text{La}}$  is the structural point defect for  $x > 0$ . With this assumption, it can be shown that  $[V_{\text{La}}] \cong \frac{16}{3}x$ , independent of temperature, for  $x$  sufficiently greater than zero [18]. We take this to be the case for  $x = x_1$ , so that the 0.53 eV activation enthalpy is an effective migration enthalpy  $H_M^{\text{eff}}$ . This value is comparable to the low end of the range of migration enthalpies of vacancies in metals [19], which like  $\text{In}_3\text{La}$  have diffusion lattices connected by near neighbor jumps.

At  $x = 0$ , there are no structural defects and  $V_{\text{La}}$  is thermally activated with  $[V_{\text{La}}] = \text{const} \cdot \exp(-H_F^{\text{eff}}/k_B T)$  in which  $H_F^{\text{eff}}$  is an effective formation enthalpy. We take this to be the case for  $x = x_2$ , as a consequence of which the difference in jump-frequency activation enthalpies at  $x_1$  and  $x_2$ , that is  $Q_2 - Q_1 = 0.81 - 0.53$  eV = 0.28 eV, can be shown to be equal either to  $H_F^{\text{eff}}$  for the six-jump cycle or vacancy conversion mechanisms or to  $\frac{2}{3}H_F^{\text{eff}}$  for the divacancy mechanism [18]. (This assumes that the same diffusion mechanism is active at both boundary

compositions.) Thus, depending on the mechanism, the effective formation enthalpy of  $V_{La}$  is 0.28(1) or 0.42(2) eV, either of which is low compared to values for other intermetallics [13,20]. Such low formation enthalpies imply very high vacancy concentrations. However, as noted previously, the structural defect concentration at  $x = x_1$  must be less than or equal to about 0.5 at. %. If this interpretation of the activation enthalpies is correct, then the effective entropy of formation of  $V_{La}$  at stoichiometry must be negative ( $\leq -3k_B$ ).

The nuclear quadrupole relaxation method for measuring tracer jump frequencies has potential limitations in its general application. There is first of all only a small number of PAC isotopes with favorable nuclear characteristics. Second, the lattice EFG must change in orientation (or magnitude) in each jump, ruling out use of the method for crystal structures with jump sublattices for which the EFG is the same at different sites. Third, inhomogeneous broadening due to lattice disorder must be sufficiently small that it does not interfere with analysis of the relaxation. Fourth, the diffusing defect (if any) must have a short residence time next to the tracer atom or else a transient EFG would be produced that adds to the lattice EFG, complicating the analysis. In the absence of tracer-defect interaction, the ratio of the residence time of a defect next to the tracer to the mean time between jumps of the tracer is  $2z[V]$ , which in the present experiments was  $\leq 0.1$ .

The nuclear quadrupole relaxation method has notable advantages in comparison with diffusion measurements. First, for crystal structures such as  $Cu_3Au$ , one can identify the sublattice on which an impurity tracer sits through the observed EFG. Second, jump frequencies are measured in thermal equilibrium whereas diffusion measurements may be disturbed by surface interactions or kinetic barriers to diffusion. Third, measurements can be made conveniently on polycrystals because the number of tracer atoms in dislocations or grain boundaries is usually very small and makes a negligible contribution to the signal. Fourth, as demonstrated by the present measurements, one can measure jump frequencies at boundary compositions in samples having two phases. This guarantees that the composition of the phase of interest remains well defined throughout the experiment, even if the mean composition of the sample changes slightly. A particularly useful application of the relaxation method appears to be the study of diffusion behavior in compounds having narrow phase fields.

Combining results of jump frequency and diffusion measurements using the same tracer offers the possibility of determining correlation coefficients experimentally. Equation (2) can be rewritten generally as  $D = gfa^2w$ , in which  $g$  is a geometrical factor dependent on the diffusion mechanism and crystal structure. In principle

one can obtain  $f$  from measurements of  $D$  and  $w$ , making it possible to determine the temperature dependence of the correlation coefficient for impurity tracers.

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