

Motion of cadmium tracer atoms in $Al_{11}R_3$ phases (R=La,Ce,Pr)

Stephanie Lage^a and Gary S. Collins^b

Dept. of Physics and Astronomy, Washington State University, Pullman, WA, USA

^a stephlage621@hotmail.com, ^b collins@wsu.edu

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Abstract. Jump frequencies of Cd tracer atoms were measured in three phases having the orthorhombic $Al_{11}R_3$ structure, with R= La, Ce, or Pr. The structure has four inequivalent Al-sites and two inequivalent R-sites. $^{111}In/Cd$ tracer atoms were observed to occupy several sites via the nuclear quadrupole interaction using perturbed angular correlation of gamma rays (PAC). Time-domain PAC spectra became damped as the temperature increased, which is attributed to nuclear relaxation caused by diffusional jumps of Cd tracer atoms leading to changes in orientations and/or magnitudes of electric field gradients (EFG's). Maximum relaxations were observed near 770 K. A method is proposed for estimating the mean jump frequency at that temperature, giving a mean jump frequency ω averaged over all sites of about 100 MHz. At still higher temperatures, damping decreased due to motional averaging, and the quadrupole perturbations evolved into unique signals having lower frequencies and corresponding in each phase to the averages of EFG tensors of all sites visited by the Cd tracer atoms. For $Al_{11}La_3$, the jump frequency at 1073 K was estimated to be 1.9 GHz. Such jump frequencies imply unusually high diffusivities in these phases.

Introduction

Measuring atomistic jump frequencies provides a microscopic means to studying diffusion in solids. Stochastic fluctuations of fields at nuclei resulting from diffusional jumps can be detected through relaxation of nuclear hyperfine interactions of tracer atoms. Such an approach was first demonstrated for perturbed angular correlation of gamma rays (PAC) in studies using $^{111}In/Cd$ tracer atoms in rare-earth indides having the $L1_2$ (Cu_3Au) crystal structure [1,2,3], and more recently in gallides and aluminides [4]. In those studies, tracer atoms jumped between near-neighbor sites on the Cu-type sublattice. Each jump was accompanied by reorientation of the local electric field gradient (EFG) by 90° , leading to decoherence in the precessions of nuclear spins of radioactive tracer nuclei. Using PAC, one measures "spin rotations" of the nuclei in the time domain. ^{111}In decays by electron capture to the second excited state of ^{111}Cd with a mean-life of 4.0 days, followed by decay to the ground state with emission of two gamma rays signaling formation and decay of a spin-5/2 intermediate state, the PAC level, that has a 120 ns mean-life. For a single site, the static perturbation function is given in the absence of inhomogeneous or dynamical broadening by

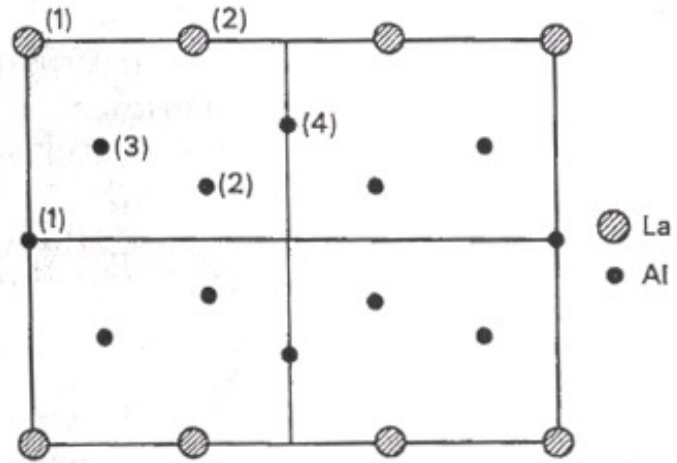
$$G_2^{static}(t) = s_0 + s_1 \cos(\omega_1 t) + s_2 \cos(\omega_2 t) + s_3 \cos(\omega_3 t), \quad (1)$$

in which the amplitudes s_n sum to 1 and $\omega_3 = \omega_1 + \omega_2$. The observed fundamental frequency ω_1 and second harmonic ω_2 are functions of the principal component of the EFG tensor and EFG asymmetry parameter, respectively V_{zz} and $\eta \equiv |(V_{xx} - V_{yy})/V_{zz}|$. When there is at least a 3-fold axis

of symmetry about the principal z -axis, $\eta = 0$, $\omega_2 = 2\omega_1$, and $\omega_1 = \omega_0 \equiv \frac{3\pi}{10} \nu_Q$, with the quadrupole coupling frequency $\nu_Q \equiv eQV_{zz}/h$ expressed in terms of the quadrupole moment Q , in which e and h are the electronic charge and Planck's constant. When, in addition, there is a random directional distribution of local EFG axes, the amplitudes are in the proportions $s_0 : s_1 : s_2 : s_3 = \frac{7}{35} : \frac{13}{35} : \frac{10}{35} : \frac{5}{35}$. For the general case $\eta \neq 0$, analytic expressions exist to determine the coupling frequency ν_Q and asymmetry parameter η from experimental values of ω_1 and ω_2 [5].

The orthorhombic $\text{Al}_{11}\text{Ce}_3$ crystal structure (oI28) is shown in Fig. 1 [6]. It has four inequivalent Al-sites and two inequivalent R-sites (R=rare earth). Due to the low crystal symmetry, none of the six sites has $\eta = 0$, and EFG axes at the six sites are not generally aligned along crystal axes. Diffusional motion reported below is assumed to occur via a vacancy mechanism owing to the similar size of La and Al atoms and close-packed nature of the structure. In the vacancy mechanism, tracer atoms exchange with vacancies on neighboring sites. Considering the local neighborhoods of the sites, jumps will most frequently be between different sites, leading to fluctuations in magnitudes as well as orientations of EFGs. Even for jumps between the same kind of site (for example, jumps between the two Al(2) sites above and below the horizontal center line in Fig. 1), there will be reorientation of the EFG tensor, leading to nuclear relaxation. Jump frequencies between pairs of sites will be assumed to be thermally activated, with the mean jump frequency w (inverse of the mean residence time) for each site-pair given by $w = w_0 \exp(-Q/k_B T)$ in terms of the activation enthalpy Q and frequency prefactor w_0 for that particular pair.

An overview of the experiment and principal results is as follows. $^{111}\text{In}/\text{Cd}$ tracer atoms were found to typically occupy 3-4 sites in each phase studied, although, due to the complexity of the crystal structure, it was not possible to identify observed signals with specific sites. However, measurements at elevated temperature exhibited nuclear relaxation of all signals. Maximum relaxation was observed at about 770 K in all three phases, at which temperature we conjecture that the mean jump frequency averaged over all jumps, w , is approximately equal to the average coupling frequency, $\langle \nu_Q \rangle$, of the different signals. At still higher temperatures, a new, unique, quadrupole interaction signal emerged that is attributed to a motional average of the static EFG tensors explored by tracer atoms during their motions, weighted by their residence times during visits to each site. Such a signal must appear when jump frequencies are so high that quadrupole moments cannot precess through an appreciable angle before a new jump occurs.



Unit cell of $\text{La}_3\text{Al}_{11}$. Section $x=0$.

Fig. 1. Half of the unit cell of $\text{Al}_{11}\text{La}_3$, showing four inequivalent Al-sites and two inequivalent La-sites. From ref. [6].

Nuclear relaxation in PAC spectra due to stochastic fluctuations of EFG's along three orthogonal cube directions was first treated by Winkler and Gerdau [7]. Approximate forms for the perturbation function were later given by Baudry and Boyer for the more general case of a cubic crystal structure in which the EFG fluctuates among N different cube directions ($N= 3,4,7$) [8]. Better analytical approximations were developed for specific values of N by Evenson and coworkers [9] and full, numerical fits have been carried out [1]. To guide the interpretation of relaxation in the present experiments, we shall adapt the approximate forms obtained by Baudry and Boyer [8] for $\eta=0$ and cubic phases to the more general case of noncubic phases and $\eta \neq 0$.

Relaxation first becomes evident at low temperature as damping of the static quadrupole interaction perturbation function. Baudry and Boyer showed that the dynamically relaxed perturbation function is given in terms of the mean jump frequency w in good approximation by

$$G_2(t) \cong \exp(-wt) \cdot G_2^{static}(t) \quad (2)$$

and is independent of N . (Note that w in eq. 2 and in eq. 3 below is defined differently here than in ref. [8]). Thus, damping *increases* with temperature due to thermal activation of w in this so-called *slow fluctuation regime*. Relaxation continues to increase with temperature through the temperature dependence of w until the jump frequency becomes approximately equal to the quadrupole interaction frequency. At still higher temperatures, with greater jump frequencies, there is less and less time for the nuclear spin to precess through an appreciable angle between jumps, so that nuclear relaxation *decreases* with increasing jump frequency. In this *fast fluctuation regime*, Baudry and Boyer obtained an expression for the perturbation that can be written in the form

$$G_2(t) \cong \exp(-\lambda t) = \exp\left(-2.5 \frac{N-1}{Nw} \nu_Q^2 t\right), \quad (3)$$

in which ν_Q is the coupling frequency. As w becomes very large, the perturbation function approaches a constant (equal to 1.0) since the EFG averaged over equivalent orientations in a cubic system is zero. It can be seen that the exponent is insensitive to N . Since relaxation increases in the slow fluctuation regime (eq. 2) and decreases in the fast fluctuation regime (eq. 3), the jump frequency at which relaxation is maximum can be determined by equating arguments of the exponentials in eqs. 2 and 3, from which, using $N \cong 3-4$, one obtains $w \approx 1.3\nu_Q$. This result is applied below to estimate mean jump frequencies in the $Al_{11}La_3$ phases at temperatures where nuclear relaxation is observed to be maximum.

Experiment and results

Samples of $Al_{11}R_3$ ($R= La,Ce,Pr$) were doped by melting carrier-free ^{111}In activity with metal foils of rare-earth elements (99.9% purity) and Al (99.999% purity) under argon in a small arc-furnace. Melted samples were spheres having masses of about 80 mg. Mole fractions of ^{111}In were about 10^{-8} . X-ray measurements verified the crystal structure and confirmed that volume fractions of neighboring phases were small.

PAC spectra were measured using four counter spectrometers of standard design [10,11]. Time-coincidence spectra measured at angles of 90° and 180° were combined to obtain the experimental

perturbation function, or spectrum. Representative spectra measured for the $\text{Al}_{11}\text{La}_3$, $\text{Al}_{11}\text{Ce}_3$ and $\text{Al}_{11}\text{Pr}_3$ samples are shown in Figs. 2-4. At and near room temperature, spectra could be fitted with superpositions of several static quadrupole perturbation functions. For $\text{Al}_{11}\text{La}_3$, four static signals were observed having coupling frequencies $\nu_Q = 39, 58, 69$ and 94 MHz, with corresponding EFG asymmetry parameters $\eta = 0.21, 0.21, 0.38$ and 0.89 . Note that the mean of the quadrupole coupling frequencies of the different signals is roughly 70 MHz. Site fractions changed to some extent with temperature, as shown in Fig. 5 for the four signals in $\text{Al}_{11}\text{La}_3$. This is attributed to equilibration of the ^{111}In impurities among the various sites, as observed in other work [11]. Observation of such changes in day-long measurements at temperatures of 100 - 200 C is evidence of thermally activated motion of the tracer atoms already at quite low temperatures.

The same qualitative changes with temperature were observed in all spectra. In Figs. 2-4 and in additional spectra measured at additional intermediate temperatures, damping was observed to increase until it became maximal at approximately 770 K in $\text{Al}_{11}\text{La}_3$ and $\text{Al}_{11}\text{Ce}_3$ and at 700 K in $\text{Al}_{11}\text{Pr}_3$. Above those temperatures, unique, new quadrupole interaction signals with low coupling frequencies began to emerge. For example, the spectrum shown for $\text{Al}_{11}\text{La}_3$ at 1073 K (Fig. 2, top) was fitted with a unique quadrupole interaction signal having $\nu_Q = 20.8(3)$ MHz, $\eta = 0.29(2)$ and a relaxation frequency $\lambda = 4.8(5)$ MHz. Although one is clearly in the fast fluctuation regime, the fitting form is similar to eq. 2 rather than eq. 3. It should be noted that the 20.8 MHz frequency is much lower than the 70 -MHz frequency average of static signals observed at low temperature.

The interpretation is as follows. Above the temperature at which maximum relaxation occurs, the still increasing jump frequency results in motional averaging of the EFG over all the sites that the tracer atoms visit. This results in an EFG having a reduced magnitude due to partial cancellation of EFG's in the averaging process. While the cubic relaxation model described in eq. 3 has a motionally averaged EFG equal to zero, the more complex orthorhombic structure here leads to a nonzero average. As an *ansatz*, we suppose that the perturbation function in the fast fluctuation regime is equal to the product of the perturbation function $\langle G_2(t) \rangle_{EFG}$ for the EFG tensor averaged over sites visited by the tracer atoms and the same relaxation factor as given by eq. 3, but in which the unique coupling frequency ν_Q is replaced by the average frequency $\langle \nu_Q \rangle$ for all sites visited:

$$G_2(t) \cong \exp(-\lambda t) \langle G_2(t) \rangle_{EFG} = \exp\left(-2.5 \frac{N-1}{Nw} \langle \nu_Q \rangle^2 t\right) \langle G_2(t) \rangle_{EFG}. \quad (4)$$

Based on the foregoing, we present two estimates of jump frequencies of Cd tracer atoms in $\text{Al}_{11}\text{La}_3$. At the temperature of maximum relaxation, ~ 770 K, $w \cong 1.3 \langle \nu_Q \rangle \approx 100$ MHz. At 1073 K, from $\lambda = 4.8$ MHz and $\langle \nu_Q \rangle \approx 70$ MHz, and using $N \sim 3.5$ in eq. 4, one obtains $w \cong 1.9$ GHz. These jump frequencies correspond to diffusivities of order 1.5×10^{-12} and 3×10^{-11} m^2/s if one assumes a correlation factor of the order of 1. These frequencies are high but not exceptional; they are almost as high as those observed for ^{111}Cd tracers in LaIn_3 [1,2], and consistent with the range of diffusivities reported for bcc rare-earth metals at their melting temperatures [12].

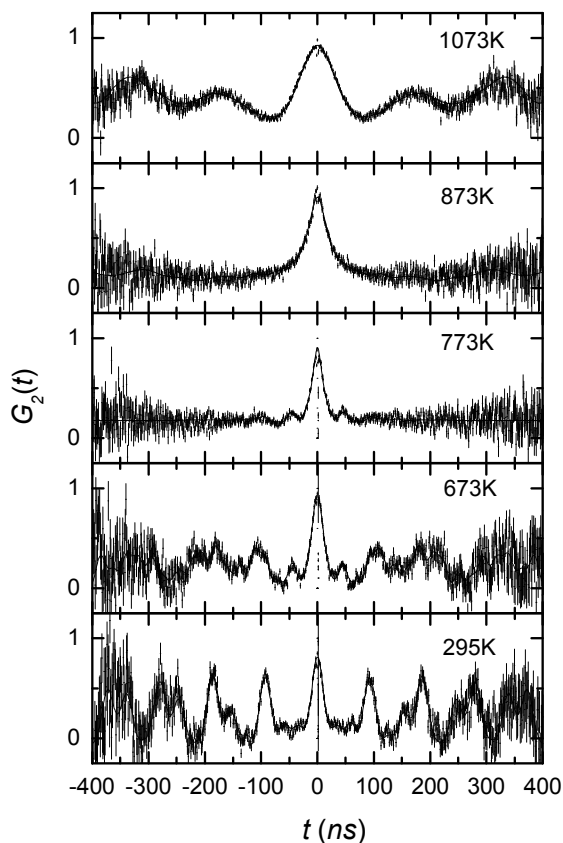


Fig. 2. PAC spectra of $^{111}\text{In}/\text{Cd}$ probe atoms in $\text{Al}_{11}\text{La}_3$ measured at the indicated temperatures. Damping is attributed to nuclear relaxation caused by jumps of Cd tracer atoms among different lattice sites. Maximum relaxation is observed at 773 K, above which a unique undamped signal emerges.

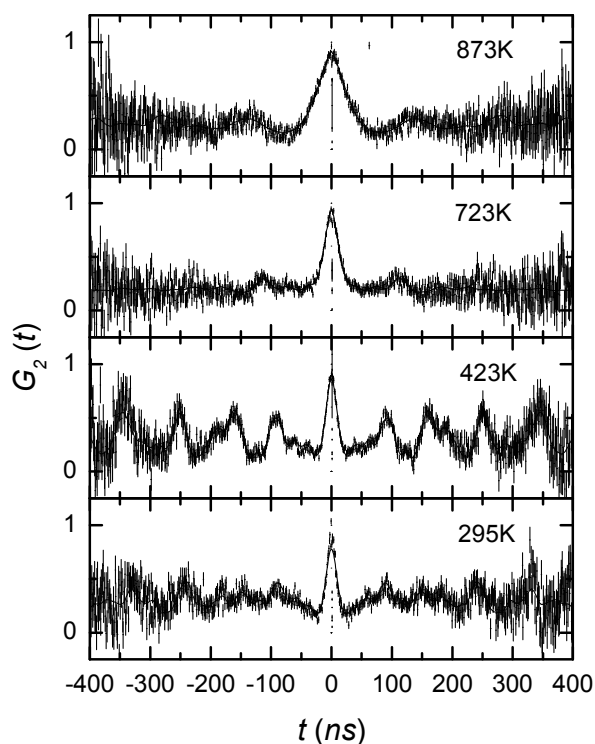


Fig. 3. PAC spectra of $^{111}\text{In}/\text{Cd}$ probe atoms in $\text{Al}_{11}\text{Ce}_3$ measured at the indicated temperatures. See caption of Fig. 2.

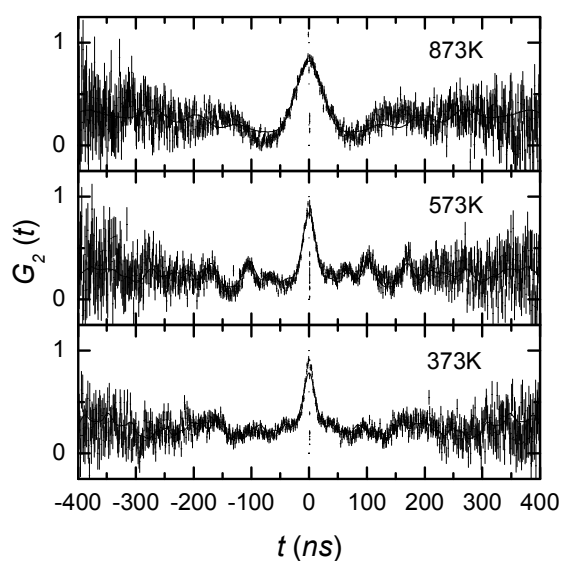


Fig. 4. PAC spectra of $^{111}\text{In}/\text{Cd}$ probe atoms in $\text{Al}_{11}\text{Pr}_3$ measured at the indicated temperatures. See caption of Fig. 2.

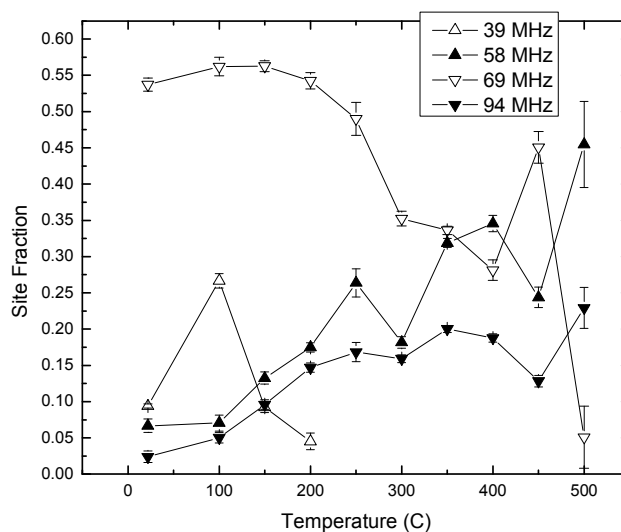


Fig. 5. Site fractions of four quadrupole interaction signals in $\text{Al}_{11}\text{La}_3$ at temperatures below 500 C, the temperature at which maximum relaxation was observed.

Discussion

Additional results and insight into the nature of damping mechanisms and diffusion processes comes from examination of the spectra.

(1) All signals in all three phases became damped as the temperature was increased toward 500 C, showing that tracers were jumping on all sublattices occupied. Observation of well-defined temperatures of maximum relaxation indicates that jump frequencies among different sites may have differed by factors of order 2 but not of order 10.

(2) The phases are believed to have a high degree of crystalline order, as evidenced by small amounts of inhomogeneous broadening at low temperature; in particular, see the spectrum for $\text{Al}_{11}\text{La}_3$ at 295 K shown in Fig. 2.

(3) Measurements for $\text{Al}_{11}\text{Ce}_3$ and $\text{Al}_{11}\text{Pr}_3$ at the lowest temperatures in Figs. 3 and 4, 295 K and 373 K, respectively, exhibit more damping than at higher temperatures. This is attributed to magnetic interactions; magnetization measurements on the $\text{Al}_{11}\text{Ce}_3$ sample using a SQUID showed a small amount of ferromagnetism at 295 K [13]. Coexistence of quadrupole and magnetic interactions leads to fractionation of PAC signals into many spectral components, giving a damped appearance that has nothing to do with either inhomogeneous or dynamical broadening. We know of no other measurements of magnetism in Al_{11}R_3 phases.

Summary and conclusions

Principal experimental observations from this study are (1) a characteristic increase and then decrease in nuclear relaxation with increasing temperature, signaling a transition from slow to fast fluctuation regimes, and (2) appearance of a unique, quadrupole interaction signal at temperatures in the fast fluctuation regime as a result of motional averaging of electric field gradient tensors over all the sites visited.

PAC measurements of jump frequencies have been made to date only for cubic systems in which there was either one jump sublattice, e.g. in $L1_2$ phases [1,2], or two jump sublattices, e.g. in phases having the Sn_7Ir_3 crystal structure [14,15]. Those measurements led to clearly defined temperature dependences of jump frequencies $w(T)$ that could be fitted to obtain jump-frequency activation enthalpies and jump-frequency prefactors. The present work shows two methods by which one can estimate mean jump frequencies of tracer atoms that are simultaneously jumping on or between several occupied sublattices—even when it is not possible to identify the sublattices with observable quadrupole interaction signals. For this purpose, a stochastic model developed for cubic systems was adapted for noncubic systems such as the present orthorhombic phases. At the temperature of maximum relaxation, the mean jump frequency is approximately given by $w \cong 1.3 \langle \nu_Q \rangle$, in which $\langle \nu_Q \rangle$ is the average quadrupole coupling frequency, weighted by the site fractions. Well above that temperature, a unique quadrupole interaction signal will be observed whose EFG tensor is an average of EFG tensors of the visited sites, also weighted by the site fractions. Consistent with the mechanism of averaging of EFG tensors, the unique signal has a lower coupling frequency than the

static frequencies of the individual sites. An estimate of the mean jump frequency w can be obtained from the measured damping frequency λ of the unique signal using eq. 4.

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