

Diffusion of ^{111}Cd probes in Ga_7Pt_3 studied via nuclear quadrupole relaxation

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Abstract Diffusion of $^{111}\text{In}/\text{Cd}$ impurity atoms was studied in Ga_7Pt_3 at the atomic level using the method of perturbed angular correlation of gamma rays (PAC). As in previous measurements on Ga_7Pd_3 , probes were observed to occupy two inequivalent Ga-sublattices. Quadrupole interaction perturbation functions for each site exhibited damping at elevated temperatures that is attributed to nuclear relaxation caused by stochastic jumps of the probe atoms accompanied by reorientation of axes of the electric field gradient tensor. Fitted relaxation frequencies, proportional to mean jump frequencies of the probe, were thermally activated. Arrhenius plots revealed jump-frequency activation enthalpies of 0.94 (8) and 0.67 (4) eV for the two sites and frequency prefactors close to 1 THz. Results were similar to those found previously for Ga_7Pd_3 , although jump frequencies are about 100 times lower in Ga_7Pt_3 .

Keywords Diffusion · Intermetallics · Nuclear relaxation · Quadrupole interaction · Nuclear quadrupole relaxation

Intermetallic compounds Ga_7Pd_3 and Ga_7Pt_3 have the cubic Ge_7Ir_3 structure, with 40 atoms per unit cell [1, 2]. There is one transition-metal site and two inequivalent, noncubic Ga-sites designated Ga(3) and Ga(4) according to the number of sites per formula unit. In a previous study of nuclear quadrupole interactions in Ga_7Pd_3 using the method of perturbed angular correlation of gamma rays (PAC) [3], impurity $^{111}\text{In}/\text{Cd}$ probe atoms were observed to occupy both Ga-sublattices, although they preferentially occupy Ga(3) sites. Quadrupole interactions were identified with sites by comparing interactions with those observed in isostructural In_7Pt_3 , in which probe atoms are not impurities and the two observed signals had the expected 3:4 ratio of site fractions. Signals were identified in the present study by observing

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characteristically large and small interaction frequencies for sites Ga(3) and Ga(4), respectively. The two Ga-sites have axially symmetric electric field gradients.

In [3] and in the present work, nuclear relaxation, which appears as “damping” in PAC spectra, is attributed to diffusional jumps of the probe atoms. Jumps on each Ga-sublattice lead to reorientation of directions of the electric field gradients (EFG). Jumps between the two sublattices lead both to reorientation and change in magnitude of the EFG. For further details of the crystal structure and jump models, see [3]. Our assumption is that diffusion occurs via a vacancy mechanism, with a small number of vacancies jumping very rapidly on the two Ga-sublattices, thereby “shuffling” atoms to near-neighbor sites. However, due to brief encounters with vacancies, no signals have been observed that might be attributed to vacancies.

The dynamically damped perturbation function is given in terms of the static perturbation function $G_2^{\text{static}}(t)$ by $G_2(t) = \exp(-\lambda t) G_2^{\text{static}}(t)$, in which λ is the relaxation frequency. The above expression applies in the slow-fluctuation regime, when λ is less than the quadrupole interaction frequency ω_Q ($\omega_Q = \frac{\pi}{20} eQV_{zz}$ for nuclear spin $I = 5/2$). Furthermore, when only the orientation of the EFG changes in a jump, as for Ga(3)–Ga(3) or for Ga(4)–Ga(4) jumps, the relaxation frequency λ is equal to the mean jump frequency, w (or inverse of the mean residence time). For a further description of relaxation due to diffusion of PAC probe atoms, see [4].

In [3], relaxation frequencies were fitted for probes on Ga(3) and on Ga(4) sites and found to be thermally activated according to $\lambda = \lambda_0 \exp(-Q/k_B T)$, in which λ_0 is a frequency prefactor and Q is the jump-frequency activation enthalpy. Both Ga₇Pd₃ and Ga₇Pt₃ phases appear as line compounds in binary phase diagrams. However, jump frequencies in other line compounds have been observed to differ appreciably for measurements made on samples prepared to have opposing boundary compositions [4]. Accordingly, measurements were made on samples having compositions of 27 and 31 at.% Pt, slightly greater and smaller than the stoichiometric composition.

Representative PAC spectra measured at different temperatures are shown in Fig. 1 (data shown for negative times are independent data completely equivalent to those shown at positive time). The perturbation functions for ¹¹¹Cd probes on Ga(3) and Ga(4) sites exhibit fundamental periods of ~22 and ~71 ns in the figure. All measurements were in thermal equilibrium except at 22°C. As can be seen, the ratio of site fractions of probes on Ga(3) and Ga(4) sites, given by the amplitudes of the two signals at time zero, is much greater than the 3:4 ratio expected if probe atoms were distributed at random on Ga-sites. This site preference of indium solutes for Ga(3) sites will be discussed elsewhere.

The temperature dependence of the relaxation frequencies is shown in Fig. 2, together with data for Ga₇Pd₃ [3], and fitted values for λ_0 and Q are given in Table 1. High-temperature values for Ga(4) in Ga₇Pd₃ that did not remain in the slow-fluctuation regime are not displayed. Some evidence has been found that thermocouples used for temperature measurement had degraded, so that temperatures for Ga₇Pd₃ data shown in Fig. 2 from [3] have been revised, leading to values for relaxation parameters in the Table that differ from in [3].

Principal observations and conclusions are as follows:

1. Relaxation frequencies for Ga(4) sites are about a factor of three greater than for Ga(3) sites in both Ga₇Pd₃ and Ga₇Pt₃. This suggests a common diffusion

Fig. 1 PAC spectra in Ga_7Pt_3 , exhibiting two quadrupole interaction signals for $^{111}\text{In}/\text{Cd}$ probes on Ga(3) or Ga(4) sites, respectively, with periods ~ 22 and ~ 71 ns

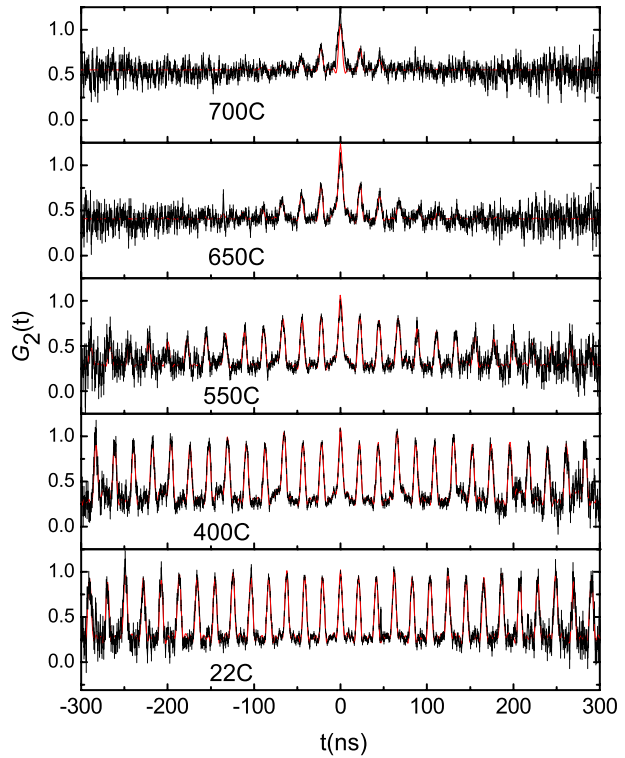
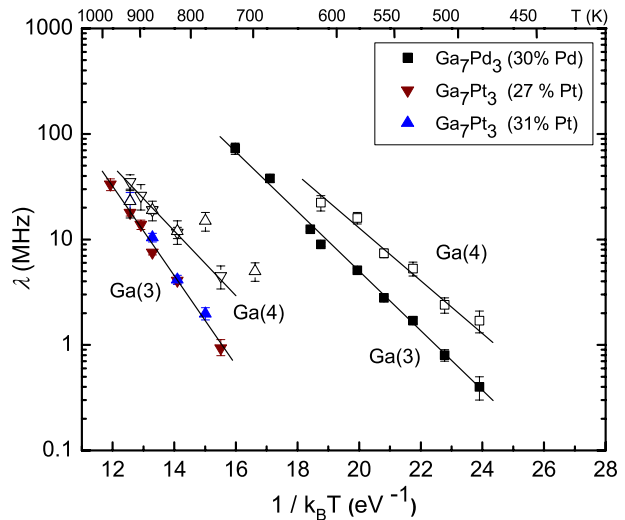


Fig. 2 Temperature dependences of relaxation frequencies for quadrupole interaction signals of indium probes on Ga(3) or Ga(4) sites for the indicated phases and compositions. Filled and open symbols identify values for Ga(3) and Ga(4) sites, respectively



mechanism in both phases. For example, the rate for Ga(3)–Ga(4) jumps might be much greater than the rates of Ga(3)–Ga(3) or Ga(4)–Ga(4) jumps, leading to a comparable ratio of relaxation frequencies. However, the Ga(3)–Ga(4) jump-distance is greatest of the three [3]. Qualitatively, jumps from site Ga(4), with

Table 1 Jump frequency activation enthalpies and frequency prefactors

Site	Ga ₇ Pd ₃ ^a (200–400°C)		Ga ₇ Pt ₃ (this work) (420–700°C)	
	λ_0 (THz)	Q (eV)	λ_0 (THz)	Q (eV)
Ga(3)	1.6 (8)	0.64 (3)	2 (2)	0.94 (8)
Ga(4)	~ 1	0.55 (5)	~ 0.2	0.67 (4)

^aRefitted data from [3] using a revised temperature scale

- a low interaction frequency, to site Ga(3), with a high interaction frequency, are expected to lead to greater decoherence of the EFG than if jumps were to another Ga(4) site. Similarly, jumps from Ga(3) to Ga(4) sites should lead to less decoherence than if the EFG reoriented in a jump without change in magnitude. These effects will tend to increase the relaxation frequency of Ga(4) and reduce the relaxation frequency of Ga(3), consistent with observation.
- The two Ga₇Pt₃ samples had average compositions of 27 and 31 at.% Pt, and were two-phase mixtures having dominant volume fractions of Ga₇Pt₃ at its two opposing boundary compositions. Significantly, Fig. 2 shows that relaxation frequencies for the two samples are indistinguishable within the precision of measurement. This is a surprise since large differences have been observed for other “line compounds” such as for In₃R phases having the L1₂ structure (R = rare earth) [4, 5].
 - Relaxation frequencies of probes in Ga₇Pt₃ can be seen to be a factor of 100 lower than in Ga₇Pd₃ at equivalent temperatures. Such a difference may arise from differences in the concentration or mobility of vacancies in the two phases. However, the difference is not correlated with lattice parameter, which is almost the same in the two phases (0.876 nm for Ga₇Pd₃ and 0.8799 nm for Ga₇Pt₃). An interesting observation is that both phases are peritectoidal, disappearing, respectively, above 733 (Ga₇Pd₃) or 1,095 K (Ga₇Pt₃). Extrapolation of relaxation frequencies for probes on Ga(3) sites to the respective peritectoidal temperatures leads to very similar values of 90 MHz for both phases.

In summary, measurements were made of relaxation of nuclear quadrupole interactions for two inequivalent Ga-sites in Ga₇Pt₃ that is attributed to diffusional jumps of PAC probe atoms. Results are similar to those observed earlier for isostructural Ga₇Pd₃, except that relaxation (and jump) frequencies are about a factor of 100 lower.

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