

# Vacancy Jumps in PdIn: Reconciling Nuclear Relaxation and Diffusion Measurements

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**Abstract.** Vacancy jump frequencies in PdIn were determined in the range 888 to 1288 K from analysis of nuclear relaxation of monovacancy signals detected by perturbed angular correlation of gamma rays. The relaxation is attributed to jumps of Pd-vacancies out of, within, or into the first neighbor shell of In/Cd probe atoms. These frequencies, measured for samples with 48.5 at.% Pd, are compared with frequencies derived from Pd-diffusivities measured for 49 at.% Pd by Hahn, Froberg and Wever [phys. stat. sol. (a)79, 559 (1983)]. Jump frequencies are found to be in excellent agreement at high temperature. An Arrhenius plot of PAC jump frequencies exhibits curvature that could be fitted well assuming a superposition of two independent jump mechanisms: one with activation energy fixed at the value 2.15 eV found by Hahn et al. and the other fitted to 0.49(14) eV. The low activation energy is attributed to a cyclic diffusion mechanism in which the first diffusion barrier has a height of 0.49 eV and in which the correlation factor is small, so that lots of jumps take place without mass transport. A possible candidate for such a jump is an In atom jumping into a Pd vacancy next to the probe.

## Introduction

Microscopic methods can help identify diffusion mechanisms in complex materials such as intermetallic compounds, where a number of alternative mechanisms may be possible. In this paper, the method of perturbed angular correlation of gamma rays (PAC) is used to determine vacancy jump frequencies in Pd-poor PdIn through relaxation of nuclear quadrupole interactions caused by stochastic jumps of vacancies near In/Cd probe atoms. The jumps cause decoherence of quadrupole interactions through reorientation of the axes of the electric-field-gradient (efg) tensor and/or through a change in magnitude of the efg.

PdIn has the CsCl-structure and a wide phase field. Deviations from stoichiometry are accommodated on the Pd-poor side by structural vacancies on the Pd-sublattice. Additional vacancies form as a result of thermal activation of defects but it can be shown that these are few under conditions of our measurements. There is some controversy as to the identity of the high-temperature equilibrium defect. Assuming it is a Schottky vacancy pair ( $V_{Pd} + V_{In}$ ) or triple-defect ( $2V_{Pd} + Pd_m$ ), formation energies were determined to be 0.9(2) and 1.6(2) eV, respectively, from Pd-vacancy concentrations measured by PAC and sample compositions [1]. Applying the methodology in ref. [1] to a sample with 48.5 at.% Pd, the vacancy concentration at 1288 K would increase to 6.2% (Schottky pair) or 5.83% (triple-defect) compared with a concentration 5.8 at.% for structural vacancies alone. Thus, for practical purposes the Pd-vacancy concentration can be taken to be constant at about 6 at.% on the Pd sublattice.

Experiments were carried out to determine vacancy jump frequencies in PdIn as a function of temperature. A partial account of this work appeared previously [2].

## Experiment and Data Analysis

A 100-mg sample of PdIn doped with the PAC probe  $^{111}\text{In}$  at the level of 10 parts-per-billion was made by arc-melting high-purity metals and carrier-free activity together in a small argon arc-furnace, followed by an annealing at 1273 K for 1 hour under hydrogen while wrapped in Mo foil to reduce evaporation of In. Since weight losses were very small, the nominal composition 48.5 at.% Pd was taken to be the actual one. PAC measurements were carried out using a four-detector spectrometer of standard design [3]. In Fig. 1 are shown PAC spectra measured at the indicated temperatures. All exhibit a prominent signal with fundamental frequency 103 Mrad/s.

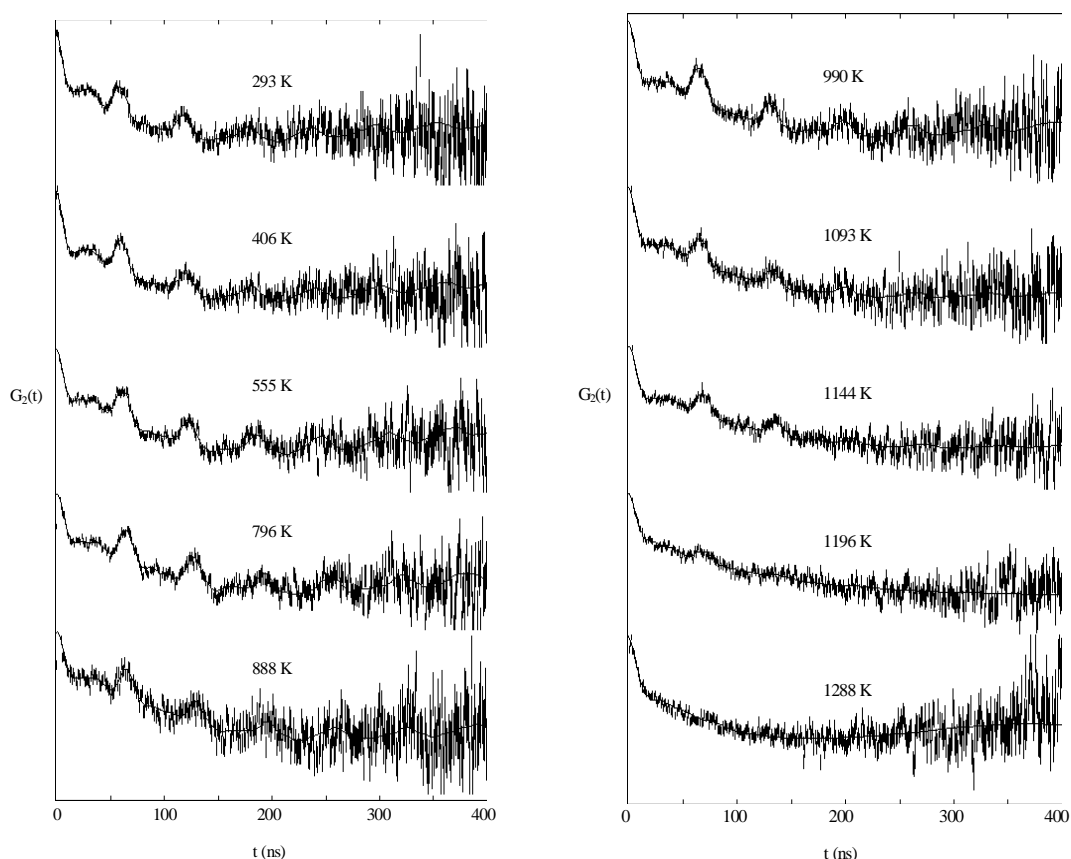


Fig. 1. PAC spectra of PdIn with 48.5 at.% Pd measured at the indicated temperatures. The prominent signal with 103 Mrad/s quadrupole interaction frequency (60-ns period) is attributed to In probe atoms with one Pd-vacancy in the first neighbor shell. Below 900 K, signals are damped by inhomogeneous broadening caused by distant defects that produce weak, static disturbances of the electric-field-gradient. Above 900 K, the signal is additionally damped dynamically via stochastic jumps of vacancies that change the orientation or magnitude of the electric-field gradient. The vacancy jump frequency is derived from the dynamical damping.

## Nuclear relaxation

Nuclear relaxation is a function of jump frequencies and vectors. In this paper, we consider only nuclear relaxation of the signal for a In/Cd probe atom that has one Pd-vacancy in the first neighbor shell at the time of creation of the nuclear state. The signal has a quadrupole interaction frequency of 103 Mrad/s at room temperature [4, 1]. For concreteness, let us suppose for now that diffusion of Pd-vacancies in Pd-poor PdIn takes place via direct jumps on the simple-cubic Pd-sublattice. Three local jumps that can give rise to relaxation of the 1V signal are shown in Fig. 2: (1) when the vacancy jumps around the probe, the efg is reoriented; (2) when the vacancy jumps away from the probe, the efg decreases to near zero, and (3) when a second vacancy jumps next to the probe, the efg increases in magnitude.

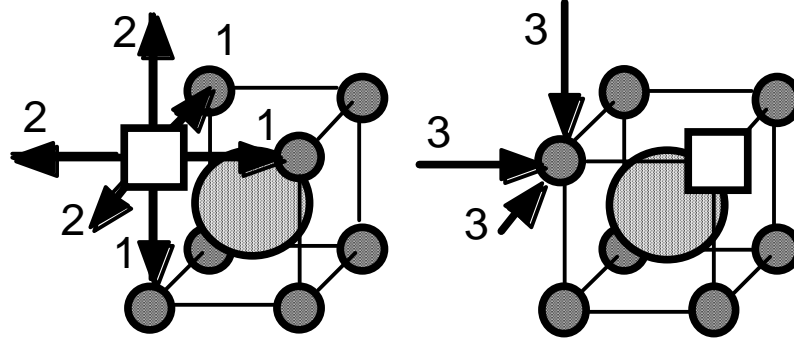


Fig. 2. Vacancy jumps on the Pd-sublattice change the efg at nearby In-probe atoms, shown by the large circle. Three kinds of jumps are possible when in the initial state the probe has one near-neighbor vacancy as shown.

In the regime in which the jump frequency  $\nu$  is less than the quadrupole interaction frequency (slow fluctuation regime), the PAC perturbation function is given in good approximation by an exponential attenuation of the static perturbation function  $G_2^{static}(t)$ :

$$G_2(t) = \exp(-\lambda t) G_2^{static}(t), \quad (1)$$

in which  $t$  is the coincidence time and  $\lambda$  is the nuclear relaxation rate.  $\lambda$  is proportional to the vacancy jump frequency  $\nu$ . For example, if the vacancy only jumps between equivalent sites (jump (1) in Fig. 2), then, to a good approximation,  $\lambda_1 = (N-1)\nu$  [5], in which  $N$  is the number of inequivalent orientations of the efg. Here,  $N=4$  for the four  $\langle 111 \rangle$  directions, so that  $\lambda_1 = 3\nu$ . Exact calculations of dynamic perturbation functions support the approximate expression given above [6, 7].

Detailed calculations are difficult when several jump mechanisms are operative at the same time, and an explicit perturbation function is not yet known for the dynamic model described above. The jump frequency  $\nu$  will be determined below from  $\lambda$  in an approximate way. Jump (2) leads to disappearance of the efg, so that the angular correlation following the jump is unperturbed. The effect is that the attenuation should be less than after reorientation, and, as a guess,  $\lambda_2 \approx \nu$ . While frequencies of jumps (1) and (2) are equal in the perfect crystal, the frequency of jump (3) is smaller by a factor equal to the vacancy concentration and will be neglected. Below, the average relation  $\lambda = 2\nu$  is used to estimate vacancy jump frequencies from the experimental relaxation rates. Spectra shown in Fig. 1 were fitted according to eq. 1, in which  $G_2^{static}(t)$  was a statically broadened perturbation function.

Relaxation rates obtained from the fits are shown in Table 1 and an Arrhenius plot of the vacancy jump frequencies is shown in Fig. 3.

T(K)	$\lambda$ (MHz)
888	0.71(90)
990	2.52(55)
1093	5.12(88)
1144	6.64(88)
1196	14.4(2.0)
1288	35.7(7.3)

Table 1. Nuclear relaxation of the 1V signal in PdIn.

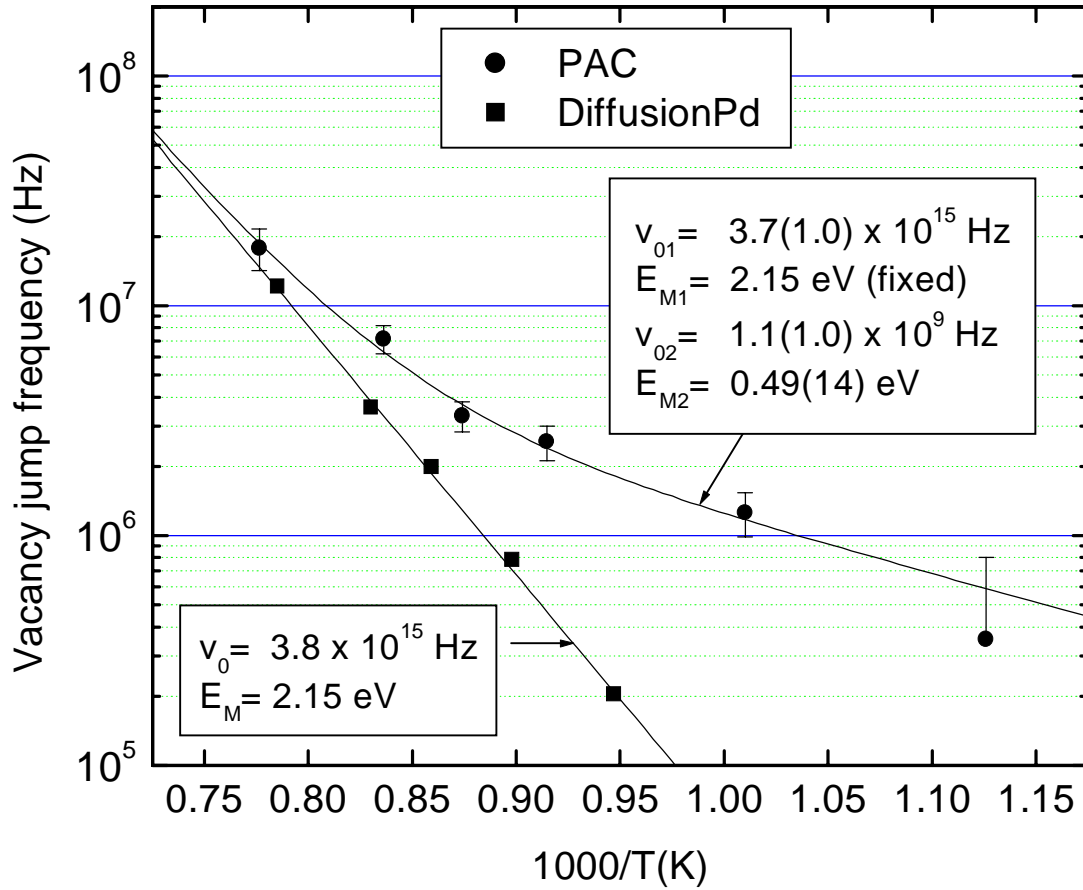


Fig. 3. Vacancy jump frequencies in PdIn determined from PAC nuclear relaxation (this work) and from Pd-diffusion [8].

Also shown in the figure are vacancy jump frequencies derived from measurements of diffusion of Pd by Hahn, Froberg and Wever [8] on a sample of PdIn with 49 at.% Pd. For a vacancy diffusion mechanism, the diffusivity can be written [9]

$$D = f[V]a^2v = f[V]a^2v_0 \exp(-E_M / k_B T), \quad (2)$$

in which  $f$  is the correlation factor,  $[V]$  is the fractional concentration of vacancies,  $a$  is the lattice parameter,  $v_0$  is a frequency prefactor and  $E_M$  is the vacancy migration energy. Here, the concentration of Pd vacancies is essentially constant with a value of 3.9 at.% over the experimental ranges of temperature,  $a$  is 3.53 Å, and, for jumps on the simple-cubic Pd-sublattice,  $f=0.653$  [9], so that  $v$  could be obtained from tabulated diffusion constants in ref. [8] using eq. 2.

As can be seen, the frequencies obtained from diffusion data fall on a straight line corresponding to a migration energy of 2.15 eV. By contrast, frequencies from the PAC data do not exhibit a simple thermally activated temperature dependence. Because PAC is sensitive to jumps that do not result in mass transport, it is natural to suppose that the greater magnitude of the frequency at low temperature is due to a second thermally activated jump mechanism. Accordingly, the PAC frequency data were fitted assuming a superposition of two simultaneous jump mechanisms. Since the two sets of frequencies approach each other at high temperature, it was assumed that the high-temperature mechanism is the same, and so its activation energy was fixed to 2.15 eV. Results of the fit are shown in the figure: The mechanism dominant at low temperature has for activation energy 0.49(14) eV and prefactor in the GHz range, a million times smaller than the prefactor for the mechanism dominant at high temperature.

It must be noted that the PAC probe is not strictly a host atom. The parent isotope  $^{111}\text{In}$  decays with half-life 2.8 days into the second excited state of  $^{111}\text{Cd}$ , which decays immediately to the PAC level. From that moment on, the probe atom is a Cd impurity whose presence can disturb jump frequencies and interact with vacancies so as to attract or repel them. Thus, the differences between frequencies as determined from PAC and diffusion data might be an artefact due to probe disturbance.

There are three reasons for believing that probe disturbance is not serious. (1) Cd and In atoms differ little in size and valence. (2) With reference to Fig. 3, there is no reason to expect that the frequencies would converge to the same value at high temperature. (3) Many diffusion mechanisms have been proposed for intermetallics (e.g., see [9, 10, 11], among which a significant number are cycles in which a series of jumps has to be made in order for the diffusion to take place without disordering the crystal. For intermetallics with the CsCl-structure, perhaps the best known example to consider is the Huntington, Elcock, McCombie six-jump cycle [9]. While the highest migration barrier relative to the starting configuration may have a magnitude of several electron-volts, the first barrier in the cycle will generally be much lower because only one antisite atom is created in the first jump. Therefore, one should expect PAC to sense many jumps that are ineffective for diffusion, and it would be surprising if they were not detected.

Thus there is good reason to accept the 0.49 eV activation energy as real. Possible explanations of the migration barrier have to consider the defect structure. In PdIn with 48.5 at.% Pd, the principal defects are structural Pd-vacancies. There are only two likely candidates for initial jumps: a Pd atom making a jump on its own sublattice into the vacancy. This is the mechanism assumed above, and the cycle is complete in the one jump, so that cannot be the jump that has an activation energy of 0.5 eV. The other candidate is an In atom jumping into a near neighbor Pd-vacancy, creating an antisite atom. This jump could be the first in a cycle or the In antisite atom could return to its original site. This jump is a likely candidate.

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