

STOCHASTIC MODEL OF PAC NUCLEAR RELAXATION CAUSED BY DEFECTS HOPPING ON A SIMPLE CUBIC LATTICE

Taylor D. Grow, Stephanie Plamondon and William E. Evenson

Department of Physics and Astronomy, Brigham Young University, Provo, Utah, USA

Gary S. Collins

Department of Physics, Washington State University, Pullman, WA, USA

A stochastic model is used to obtain an analytic approximation for the perturbation function caused by quadrupole interaction that applies when there is a fixed concentration of defects hopping on a simple cubic lattice, with the probe atom located at center of one of the cubes. A realization of this model is jumping of structural vacancies on one sublattice in the CsCl structure, with the probe atom on the other sublattice. PAC spectra obtained for Pd-poor PdIn using $^{111}\text{In}/\text{Cd}$ probes are refitted with the model perturbation function to obtain the vacancy jump frequency as a function of temperature.

Perturbed angular correlation of gamma rays (PAC) is a method well suited for measurement of nuclear relaxation rates through quadrupolar relaxation. Qualitatively, the perturbation function in the slow fluctuation regime is equal to a static perturbation function multiplied by a relaxation function of the form $\exp(-gwt)$, in which w is the stochastic relaxation frequency and g is a geometric factor of order one. A more rigorous approach is to use Blume's stochastic model [1,2], in which one considers stochastic hopping among all the hyperfine field states the system experiences, with their respective probabilities. One obtains in that way numerical expressions for perturbation functions that can be fitted with analytic approximation for practical use.

A particularly important application is in analysis of atomic diffusion in crystals. Early work focussed on models describing localized motion of defects, such as in the XYZ model of Winkler and Gerda [2,3,4] and the XYZd model that adds trapping and detrapping [5, 6, 7]. In the present work, we consider a simple diffusion model in which defects hop on a simple cubic lattice, with the hyperfine probe atom at the center of a cube, such as in the CsCl structure when defects can hop on only one of the two sublattices. Consider in particular vacancies hopping on one sublattice in a highly-ordered structure. The vacancy may make direct (second-neighbor) jumps on its own sublattice, or may execute rapidly a more complicated jump sequence that has as its end result the displacement of the vacancy without creation of other defects. As long as the residence time on the sublattice is long compared with the time necessary to complete a jump, the effect on nuclear relaxation will be the same as if the vacancy makes jumps only on its sublattice.

Jumps lead to three distinct relaxation processes: (1) a vacancy in the first atomic shell of a probe atom may jump to an equivalent site on the cube surrounding the probe, leading to reorientation of the electric-field gradient (efg) at the probe site without change in magnitude; (2) a vacancy in the first shell can jump away to the fourth shell, leading to a much smaller efg; or (3) a vacancy in shell 4 of a probe can jump into shell 1, creating a large efg. If the probe atom is not an impurity, then all jump frequencies are the same. As a consequence, the relative frequencies of jumps 1,2 and 3 are 1:1:c, in which c is the fractional concentration of defects. For the zero-vacancy site, only the third process is possible, with a rate proportional to c . For two-vacancy configurations, the primary process is the second one, transforming the configuration into a monovacancy. For the monovacancy configuration, all three processes are possible.

A ‘jump matrix’ is set up with transition rates between each of the states in the model. To minimize the number of parameters, these rates are taken relative to the hopping rate, w , for a single vacancy. The trapping rate depends on the concentration of vacancies. A full computer calculation can be done for this model for arbitrary transition rates. Our experimental data are relevant to the slow-fluctuation regime, $w \ll \omega_{1V}$. Here, ω_{1V} is the fundamental measured quadrupole frequency for the configuration of a probe with one vacancy in the near-neighbor shell (1V). When the electric-field gradient is axially symmetric (that is, $\eta=0$, see below), $\omega_{1V} = \frac{3\pi}{10} eQV_{zz} / h$, in which Q is the quadrupole moment of the PAC level and V_{zz} is the electric-field gradient.

Perturbation functions calculated in the slow-fluctuation regime were fitted to obtain simple analytic expressions. The resulting function $G_2(t)$ obtained can be written as a sum of dynamically relaxed functions for monovacancy, vacancy-free and two double-vacancy signals:

$$G_2(t) = pe^{-8wt} G_2(1V) + qe^{-wt} G_2^{static}(0V) + re^{-1.3wt} G_2^{static}(2Va) + re^{-1.3wt} G_2^{static}(2Vb) \quad (1)$$

in which site-fractions $p = 8c/(1+8c+16c^2)$, $q = 1/(1+8c+16c^2)$, and $r = 16c^2/(1+8c+16c^2)$ are functions of the concentration of vacancies, c . From the calculation, each of the four signals is multiplied by an exponential relaxation function that contains an empirical constant. Examination of the empirical constants shows that the monovacancy signal is much more rapidly damped for a given value of w than the 0V or 2V signals. This is because a greater number of relaxation processes can affect the monovacancy signal. In greater detail, the jump processes are found to also modify the form of the monovacancy perturbation function itself through phase shifts in each of the oscillatory terms that depend on the ratio of w to the quadrupole interaction frequency ω_{1V} ; specifically,

$$\begin{aligned} G_2(1V) = & \frac{1}{5} + \frac{13}{35} \frac{\cos(\omega_{1V}t + 0.25 \frac{6w}{\omega_{1V}})}{\cos(0.25 \frac{6w}{\omega_{1V}})} \exp\left(-\frac{1}{2}(\sigma_{1V}t)^e\right) + \\ & + \frac{10}{35} \frac{\cos((2 - \eta'_{1V})\omega_{1V}t + 0.4 \frac{6w}{\omega_{1V}})}{\cos(0.4 \frac{6w}{\omega_{1V}})} \exp\left(-\frac{1}{2}((2 - \eta'_{1V})\sigma_{1V}t)^e\right) + \\ & + \frac{5}{35} \frac{\cos((3 - \eta'_{1V})\omega_{1V}t + 0.35 \frac{6w}{\omega_{1V}})}{\cos(0.35 \frac{6w}{\omega_{1V}})} \exp\left(-\frac{1}{2}((3 - \eta'_{1V})\sigma_{1V}t)^e\right) \end{aligned} \quad (2)$$

Eq. 2 reduces to the static perturbation function for the monovacancy signal in the limit $w \rightarrow 0$. The three frequency harmonics in eq. 2 are in the proportions $1 : (2 - \eta'_{1V}) : (3 - \eta'_{1V})$, in which the parameter η'_{1V} allows for an apparent asymmetry of the electric-field gradient tensor due to inhomogeneous broadening. Included in eq. 2 are frequency distribution widths σ_{1V} that account for inhomogeneous broadening due to unresolved weak quadrupole interactions caused by distant defects. The exponent e in eq. 2 reflects the detailed shape of the frequency distribution. PAC spectra for PdIn at low temperature described below were fitted best using an empirical value $e=1.5$. This broadening can be treated as static because nuclear relaxation varies as the square of the quadrupole interaction frequency and therefore distant defects produce negligible relaxation. Below, results of fits of PAC spectra for PdIn

having about 48.5 at.% Pd are presented. In off-stoichiometric, Pd-poor PdIn, the principal structural defects are vacancies on the Pd-sublattice and there are essentially no defects on the In-sublattice. Relative to an $^{111}\text{In}/\text{Cd}$ probe on the In-sublattice, the vacancies are in atomic shells 1 and 4. The quadrupole interaction frequencies for vacancies have been measured to be 103 Mrad/s in shell 1 [8, 9] and 6 Mrad/s in shell 4 [9]. Thus, relaxation due to motion of defects in shells 4 and greater is completely negligible. The fractional broadening of each frequency component of the perturbation function is assumed to be the same, with the lineshape of the broadening controlled by the exponent e . The other three perturbation functions are less affected by relaxation than the monovacancy function, and so are approximated by a product of their static forms with exponential relaxation functions. There are two distinct double-vacancy configurations with significant site fractions. For configuration 2Va, for example, which has a non-axially symmetric efg,

$$\begin{aligned} G_2^{static}(2Va) = & \frac{1}{5} + \frac{13}{35} \cos(\omega_{2Va}t) \exp\left(-\frac{1}{2}(\sigma_{2Va}t)^e\right) + \\ & + \frac{10}{35} \cos((2 - \eta'_{2Va})\omega_{2Va}t) \exp\left(-\frac{1}{2}((2 - \eta'_{2Va})\sigma_{2Va}t)^e\right) + \\ & + \frac{5}{35} \cos((3 - \eta'_{2Va})\omega_{2Va}t) \exp\left(-\frac{1}{2}((3 - \eta'_{2Va})\sigma_{2Va}t)^e\right) \end{aligned} \quad (3)$$

in which the efg asymmetry parameter is fitted via parameter η'_{2Va} . To illustrate the form of the total perturbation function, Fig. 1 shows a detailed simulation for $w/\omega_{1V} = 0.0167$. The figure was calculated using hyperfine parameters that roughly describe signals in PdIn, but in the absence of static broadening. Also shown is the analytic approximation given in eq. 2, which can be seen to reproduce the exact calculation very well.

PAC spectra for PdIn containing about 48.5 at.% Pd and measured between room temperature and 1290 K were fitted using eqs. 1-3 and perturbation functions similar to eq. 3 for configurations 0V and 2Vb. The same spectra were previously fitted [10] using an empirical function for relaxation of the 1V component alone via an exponential prefactor $\exp(-2wt)$. Results of the present fits of data between 990 and 1290 K are shown in Fig. 2 as an Arrhenius plot of the vacancy jump frequency. Fits of measurements at temperatures lower than 990 K, where w was less than about 10^5 Hz, were less successful, with w sometimes fitted with unphysical, negative values. This is attributed to difficulty in fitting relaxation in spectra with an appreciable amount of inhomogeneous broadening. Also shown in the figure is a straight line representing results of Pd tracer diffusion measurements in samples having 49 at.% Pd [11]. In such a sample, there is a large fixed and known concentration of Pd-vacancies, so that the vacancy jump frequency can be derived from the diffusivity. As can be seen, the jump frequencies observed via PAC are close to those deduced from the diffusion measurements at high temperature, with an increasing difference at low temperature.

Curiously, the jump frequencies deduced for the four measurements at the highest temperatures by the two methods agree excellently within the precision of measurement. This is surprising since one might have expected a factor of 4 difference like the ratio of coefficients in the exponential damping functions. The reason why the values agree is not clear. It has to be assumed that the present method of fitting is more reliable than the one used in ref. [10] because all signals are fitted, in particular both the 1V and 0V signals that have large site fractions. Concerning the discrepancy between the PAC and diffusion frequencies, there was some discussion in ref. [10]. There it was suggested that the upward curvature in the Arrhenius plot might be caused by two competing diffusion mechanisms,

only one of which contributes to atom transport. In particular, complicated jump cycles such as the Huntington-Elcock six-jump cycle in the CsCl structure [12] may contribute to PAC relaxation without mass transport when they are incomplete (small correlation factor at low temperature.)

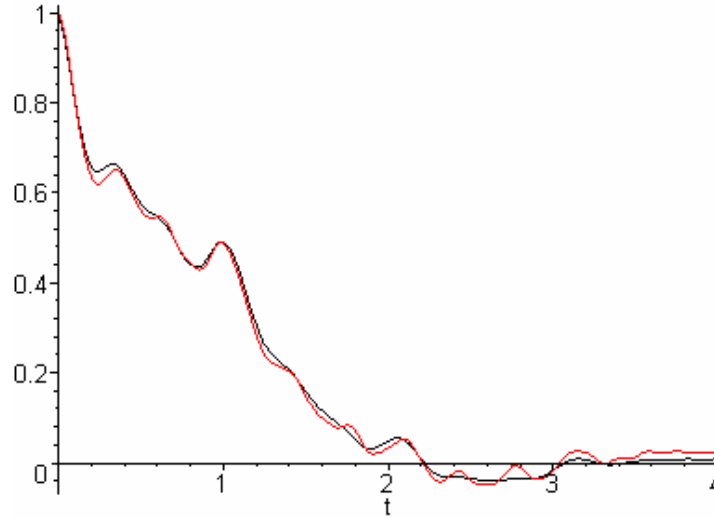


Fig. 1. Comparison of numerical perturbation function and fitted analytic approximation for $w/\omega_v = 0.0167$.

The model embodied in eqs. 1-3 assumes that the probe atom is a host atom that creates no disturbance. The experimental data for PdIn, however, involves measurements using the 247 keV level of ^{111}Cd , formed immediately following decay of ^{111}In by electron-capture. Thus, although the parent In-probe is not an impurity, the Cd-probe is. It should be recognized that such a disturbance could affect all three relaxation jump-mechanisms: (1) The jump-frequency of a vacancy to an equivalent site in the first shell of the probe may be modified by disturbances of interatomic potentials due to the probe. (2) The jump-frequency of a vacancy from the first shell into the fourth shell may be modified, especially by a binding energy between a vacancy and the impurity probe. (3) The jump-frequency of a vacancy into the first shell from the fourth shell may be modified by changes in interatomic potentials. Our expectation is that these disturbances are small because of the similarity between the chemistry of the Cd-daughter and In-parent probes, but it must be recognized that the disturbances are at present unknown and might be significant.

In summary, a perturbation function has been developed that describes nuclear relaxation due to motion of defects on a simple cubic lattice at a probe centered in one of the cubes.

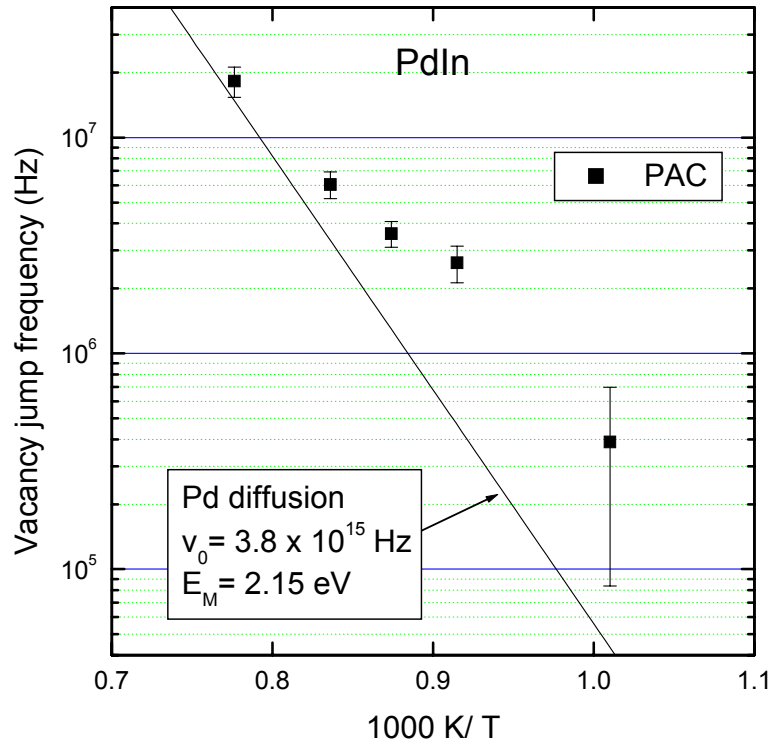


Fig. 2. Jump frequencies of Pd-vacancies in PdIn determined by fitting PAC spectra (squares) or by diffusion (straight line).

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