

STOCHASTIC VACANCY MOTION IN B2 INTERMETALLICS DETECTED BY PAC

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ABSTRACT

Using perturbed angular correlation of gamma rays (PAC), nuclear relaxation has been detected at high temperature in highly ordered B2 intermetallics that is attributed to stochastic motion of vacancies near $^{111}\text{In}/\text{Cd}$ probe atoms. The relaxation is of quadrupole interaction signals due to transition-metal vacancies in the first atomic shells of the probes. Possible relaxation mechanisms are reorientation of the vacancy with respect to the probe, detrapping of the vacancy, or trapping of a second vacancy. The relaxation reaches values of 10 MHz at temperatures of 1500K, 1200 K and 1170 K, respectively, for NiAl, FeAl and PdIn. For NiAl and FeAl, the onset of relaxation is abrupt, suggesting an activation enthalpy for the associated vacancy motion of several electron-volts. For PdIn, the relaxation has an activation enthalpy of 1.00(19) eV, a value significantly lower than might be expected naively on the basis of diffusion data. This difference gives insight into vacancy motion and diffusion mechanisms in PdIn.

INTRODUCTION

The microscopic technique of perturbed angular correlation of gamma rays (PAC) has been shown to be well suited to study point defects in solids by its ability to resolve quadrupole interaction signals caused by the different defects.[1,2] The quadrupole interactions arise from electric-field gradients produced by the defects. Over the past decade we have been studying point defects in highly-ordered B2 intermetallics. Earlier measurements of properties of thermal defects were made on samples after quenching.[3] The most important measurable for quenched samples is the site-fraction of vacancies next to the probe atoms, which is proportional to the fractional concentration of vacancies in the lattice. More recently, we have begun measurements of vacancy site-fractions at high temperature. These help to determine properties of equilibrium defects while avoiding complications introduced by quenching we have described elsewhere.[4]

High-temperature measurements on NiAl, FeAl and PdIn samples all give evidence of nuclear relaxation that is attributed to motion of vacancies near the probe atoms. In the slow-fluctuation regime investigated here, the nuclear relaxation rate λ is proportional to the vacancy jump rate w : $\lambda = aw$. The constant of proportionality a is of order unity and depends on the jump-vector and on the direction and magnitude of the electric-field gradient before and after the jump. Since the only strong quadrupole interactions in these systems are caused by one or more vacancies in the first shell [5], the relaxation must be due to motion of vacancies into, out-of, or within the first shell. In the present paper we present our first measurements and outline possible mechanisms to explain the observed relaxation.

EXPERIMENTS AND RESULTS

Samples of NiAl, FeAl and PdIn were made by arc-melting high-purity metals together with ^{111}In activity. Typical samples contained 100 mg with ^{111}In at the part-per-billion level.

Measurements were made using a high-temperature PAC oven [6] and a standard four-detector spectrometer.[2] Spectra exhibited signals attributed to single transition-metal vacancies in the near-neighbor shells of the In probe atoms.[5] In Fig. 1 are shown spectra from measurements on a NiAl sample with 50.05 at.% Ni. The measurement at 296 K exhibits quenched-in single vacancies, with a quadrupole interaction having a characteristic period of about 50 ns. The measurements at higher temperature are in equilibrium and show two features of interest. (1) The signal amplitude of the vacancy signal, equal at time zero to the site fraction of probes having a near-neighbor vacancy, increases with temperature, as expected for thermal activation of defects. (2) Measurements at temperatures above 1302 K exhibit increased “damping”. The increased damping is not correlated with the concentration of defects and therefore is not caused by inhomogeneous broadening. It is instead attributed to atom movement.

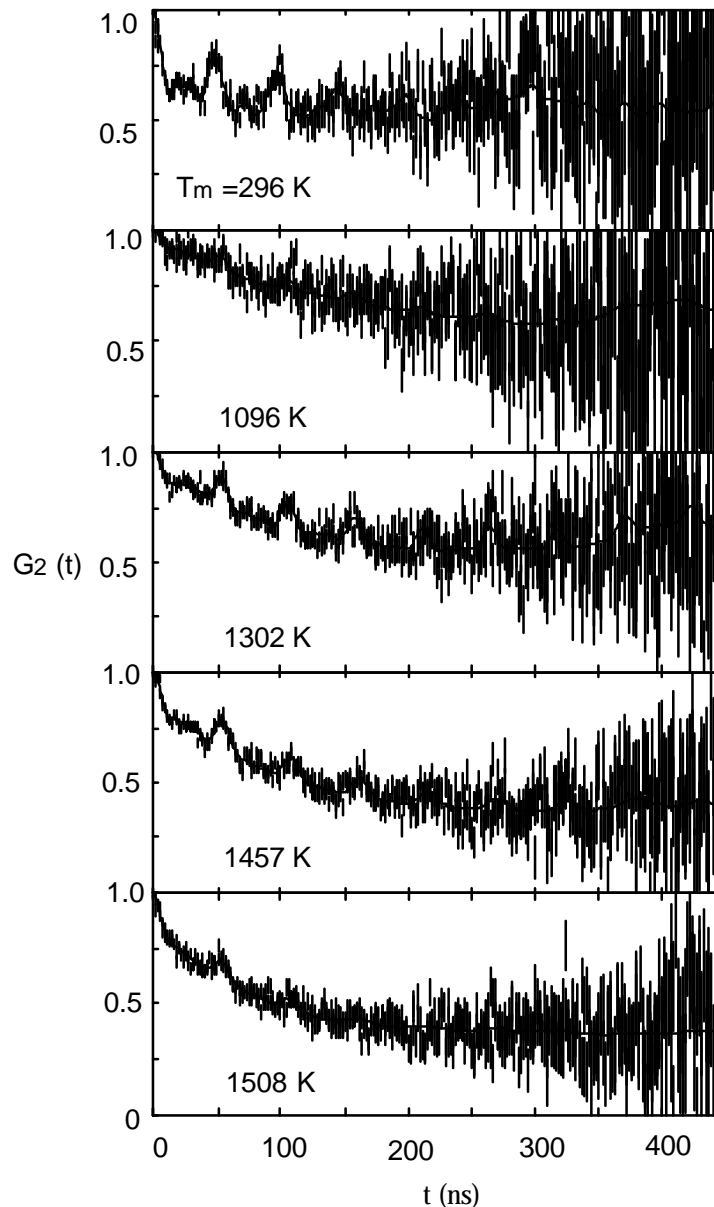


Fig. 1. PAC spectra of NiAl measured at the indicated temperatures. The 50-ns signal is caused by single vacancies next to the probe atoms. The measurements from 1096 to 1508 K are in equilibrium and exhibit nuclear relaxation attributed to vacancy jumps above 1302 K.

The perturbation function $G_2(t)$ for the single vacancy was fitted using

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

in which an exponential relaxation function multiplies the static perturbation function [2] for the vacancy. Fits yielded a relaxation rate $l = 10$ MHz at 1508 K.

Measurements on FeAl with 52.7 and 54.7 at.% Fe (not shown) were more complicated to analyze because the thermally activated vacancy concentration reaches values in excess of 1%, leading to a temperature-dependent inhomogeneous broadening. However, an additional, rapid increase in broadening of the monovacancy signal was observed at 1200 K that is attributed to motional relaxation, with the relaxation rate again equal to about 10 MHz.

PAC spectra of a PdIn sample having 48.5 at.% Pd are shown in Fig. 2. Unlike for the NiAl and FeAl samples, the Pd-poor composition leads to the presence of constitutional Pd-vacancies with a fractional concentration of about 6% on the Pd-sublattice. Such a large concentration is far in excess of any additional thermal vacancies created at high temperature. Thus, the Pd-vacancy concentration remains constant to a good approximation, so that the signal damping in excess of that observed at low temperature can only be attributed to nuclear relaxation. As can be seen, there is a significant increase in relaxation over the range 1144 K to 1288 K.

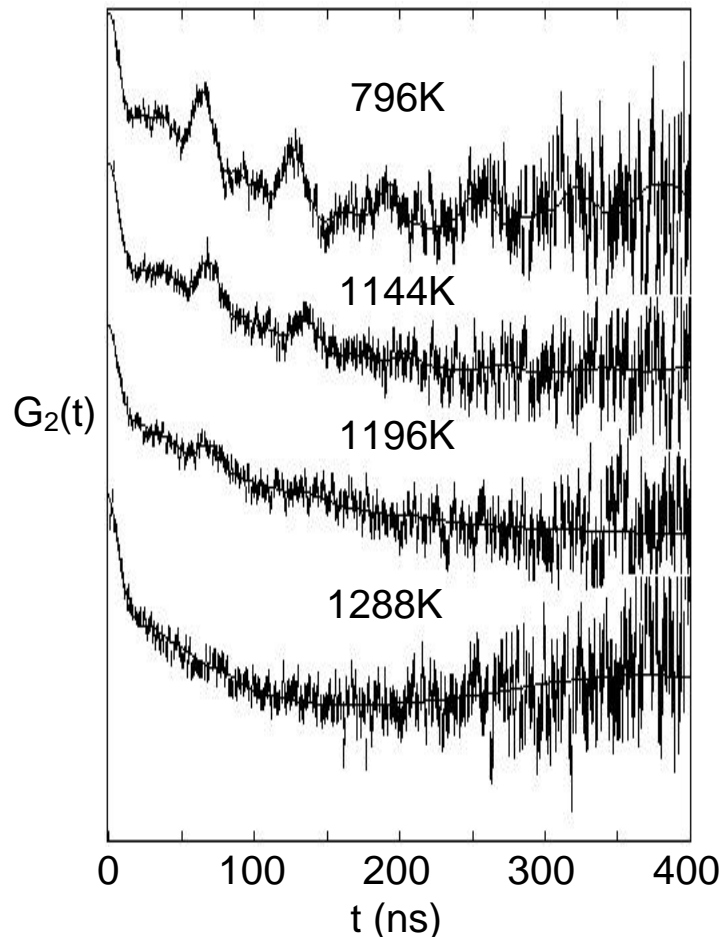


Fig. 2. PAC spectra of PdIn with 48.5 at.% Pd measured at high temperature. The signal with 60-ns period is caused by one Pd-vacancy in the near-neighbor shell of In probe atoms.

Relaxation rates for the 48.5 at.% sample obtained from fits of spectra like those in Fig. 2 are plotted in Fig. 3 versus reciprocal temperature. The relaxation is seen to be thermally-activated, with a fitted enthalpy of 1.00(19) eV and prefactor of the order of 10^{12} Hz.

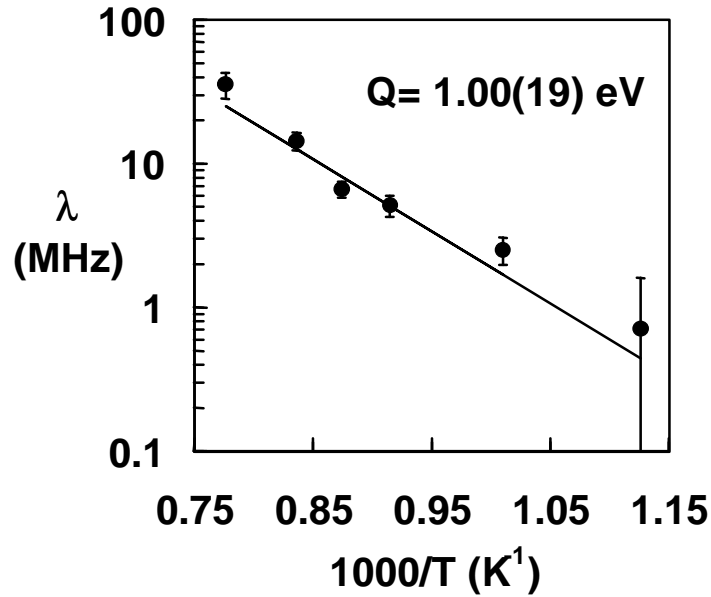


Fig. 3. Relaxation rate of the single-vacancy signal in PdIn.

DISCUSSION

In the perfect B2 structure, the In probe atom sits on the Al- or In-sublattice, surrounded by 8 transition-metal atoms. Two conditions are required to observe relaxation of the single-vacancy signal: (1) Obviously, one vacancy must be present next to the probe at the time of the nuclear decay or the characteristic vacancy signal will not be observed. (2) Either that vacancy or some other vacancy must move in the near-neighbor shell of the probe atom.[7] Three possible processes are illustrated in the Fig. 4.

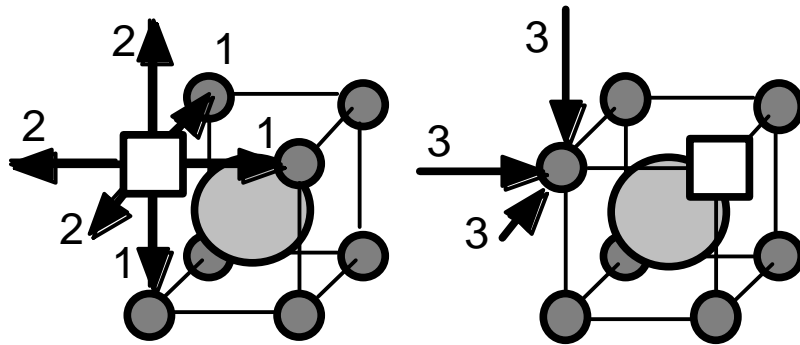


Fig. 4. Three vacancy-jump processes leading to relaxation of the single-vacancy signal: reorientation (1), detrapping (2), and trapping of a second vacancy (3). The probe atom (large circle) is surrounded by 8 transition-metal atoms (circles) or vacancies (squares) in the first atomic shell.

The processes are named in a way that is appropriate for an impurity probe that attracts and binds transition-metal vacancies, such as In in NiAl and FeAl, and described as follows:

1. Reorientation of the axis of the electric-field gradient (efg) tensor occurs if the original vacancy jumps to an equivalent site in the first shell. The changes in the direction of the axis lead to rapid decoherence of the nuclear precession. When this is the only active relaxation process, it can be analyzed using the $N=4$ state relaxation model, in which the efg reorients stochastically among the 4 equivalent $\langle 111 \rangle$ directions in the crystal structure.[8] A detailed theoretical perturbation function has been calculated [8] which can be approximated reasonably well using eq. 1 with $l = 2.9 w$.
2. Detrapping occurs if the vacancy jumps away from the probe atom. In this case, the interaction frequency decreases suddenly from a large value to near zero, with less rapid decoherence of the precession ($l @ w$).
3. Trapping of a second vacancy in the first shell during the lifetime of the probe's nucleus results in an increase in the magnitude of the interaction frequency [5] and a change in orientation of the efg axis. For this process, we guess that $l \sim (2-5)w$.

The relative importance of the three processes will vary with the type of system studied. In general the rates for the three processes will be different and have different activation enthalpies. The general situation in which more than one process is active has not been treated in detail. However, there are special cases of interest as follows:

Host-probe system. For the ^{111}In probe in PdIn, to a first approximation the probe is a host atom and jumping rates should be the same as elsewhere in the lattice.[9] If Pd-vacancies make next-near-neighbor (NNN) jumps on their own sublattice, as drawn in Fig. 4, then there will be a single activation energy: the migration enthalpy of a vacancy to make the jump. Pd self-diffusion measurements in PdIn with 49 at.% Pd by Hahn, Froberg and Wever yielded an activation enthalpy of 2.15(3) eV.[10] Since the concentration of Pd-vacancies was nearly constant in their measurements, the activation enthalpy for Pd-vacancy formation could be taken to be zero. Assuming the NNN diffusion model, Hahn et al. therefore attributed the 2.15 eV activation enthalpy to the migration enthalpy of Pd-vacancies via the NNN jump. Accepting their model, one should expect their activation enthalpy to agree with our measurement of 1.0(2) eV, which is clearly not the case. We believe the discrepancy points to the invalidity of the NNN diffusion model. We offer two possible explanations: (1) If diffusion takes place via near-neighbor jumps, then vacancies must be created on the In-sublattice that will require some activation enthalpy for formation. Then the diffusion enthalpy (2.15 eV) should be equal to the sum of the migration enthalpy (1.0 eV) and an effective formation enthalpy for In-vacancies. (2) If diffusion takes place via vacancy-jump cycles that require steps with increasing activation enthalpies for successive jumps, such as the Huntington-McCombie-Elcock 6-jump cycle [11], then a lower activation enthalpy should be observable for jump cycles in which the vacancy returns to its starting point without completing a cycle. Those jumps will contribute to microscopic relaxation but not to diffusion. In the language of diffusion theory, the quadrupolar relaxation observed here ignores correlation factors.

Strong trapping: reorientation dominant. Tightly bound vacancies can only hop around the probe atoms. Trapping and detrapping rates will then be much smaller than the reorientation rate, so that relaxation via reorientation will dominate. A good realization of this case is relaxation of In probes in CeO_2 caused by hopping of a tightly bound, trapped oxygen vacancy.[12]

Weak trapping. The situation for ^{111}In probes in NiAl or FeAl is intermediate between the above two cases. Here the binding enthalpy of the vacancy to the probe (0.18 eV to ^{111}In in NiAl [3,6]) is small compared to the vacancy migration enthalpy, of order 2 eV, but the relative rates of the three processes may be modified in uncertain ways. The most salient influence is atomic misfit of the oversized In-probe in NiAl and FeAl. At first sight it may appear that the reorientation rate should increase at the expense of the detrapping rate, but it is not obvious which process probe misfit will enhance.

CONCLUSION

PAC was used to detect nuclear relaxation in three B2 intermetallic compounds that has to be attributed to motion of transition-metal vacancies. For PdIn, an activation enthalpy of 1.0(2) eV was determined for the vacancy jump rate. This enthalpy is significantly smaller than expected on the basis of diffusion measurements using a particular diffusion model. We proposed two alternative explanations.

It has been demonstrated at least for PdIn that activation enthalpies of vacancy jump rates measured on an atomic scale using PAC give information complementary to macroscopic diffusion measurements. In particular, quadrupolar relaxation is insensitive to correlation factors that are important in the analysis of diffusion measurements and therefore may give a truer estimate of total vacancy jump rates in intermetallic compounds.

ACKNOWLEDGMENT

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