

## **ATOMIC DEFECTS AND DISORDER IN MECHANICALLY-MILLED INTERMETALLIC COMPOUNDS \***

GARY S. COLLINS + AND PRAVEEN SINHA

Department of Physics, Washington State University, Pullman, WA 99164-2814, USA

**Keywords:** point defects, defect concentrations, vacancy, antisite atom, mechanical-milling, lattice disorder, intermetallic compound, perturbed-angular-correlation of gamma rays, PAC.

**Abstract.** Local configurations of point defects were detected with atomic-scale resolution in mechanically-milled PdIn and NiAl through nuclear quadrupole interactions they induce at neighboring sites of  $^{111}\text{In}$  probe atoms, using the technique of perturbed angular correlation of gamma rays (PAC). For PdIn, signals were detected which could be attributed to Pd-vacancies, Pd-antisite atoms and In-vacancies, as in previous studies of annealed or quenched PdIn. In addition, a new signal has been observed which is attributed to high-energy In-antisite atom defects next to the In probe. Concentrations of Pd-vacancies and In-antisite atoms were determined from measured site fractions and monitored as a function of milling time. For PdIn, milling in a WC vial under argon using a Spex 8000 mill leads to a Pd-vacancy concentration that increases from zero and saturates after 30 minutes at a value of 3.5(5) at.%. Such large vacancy concentrations make a contribution to the stored excess enthalpy of about  $4.4 \text{ kJ mol}^{-1}$ . The In-antisite atom concentration reached  $\sim 4$  at.% after 2 hours of milling, providing evidence of gradual disordering of the B2 structure. Spectra for NiAl exhibit larger vacancy site fractions attributed to binding with the impurity In probe.

### **Introduction.**

Mechanical milling (or grinding) is interesting from a fundamental point of view because it frequently leads to extensions of phase boundaries and/or transformations to nonequilibrium phases.. Such transformations have generally been attributed to production of lattice defects that increase the enthalpy of the equilibrium phase to the point that it exceeds the free energy of some nonequilibrium phase. What defects are responsible? In previous studies of milled intermetallic compounds, excess enthalpies of the order of  $10 \text{ kJ mol}^{-1}$  have been measured [1] but have generally been attributed to grain boundaries.[1,2]

The present study was undertaken to investigate whether or not point defects such as lattice vacancies and antisite atoms contribute significantly to the excess stored enthalpy in milled materials. Processing of intermetallic compounds in a high-energy vibrator mill such as the Spex 8000 used in this work typically leads to grain sizes of about 10 nanometers and lattice strains of several percent. Because the particle sizes are so small, it is not generally possible to apply "standard" techniques for measuring concentrations of point defects such as lattice vacancies: for example, mass-density measurements become uncertain due to small particle size and/or sample porosity, and in positron annihilation measurements the positrons may tend to trap at grain boundaries and interfaces between grains that are present in high concentration rather than at vacancies within the grains.

To measure the concentrations of such defects we use the technique of perturbed angular correlation of gamma rays (PAC), which can discriminate microscopically among the different defects. Intermetallic compounds PdIn and NiAl were chosen for study because they have the simple B2 (CsCl) structure and are normally highly ordered, which limits the number of potential point

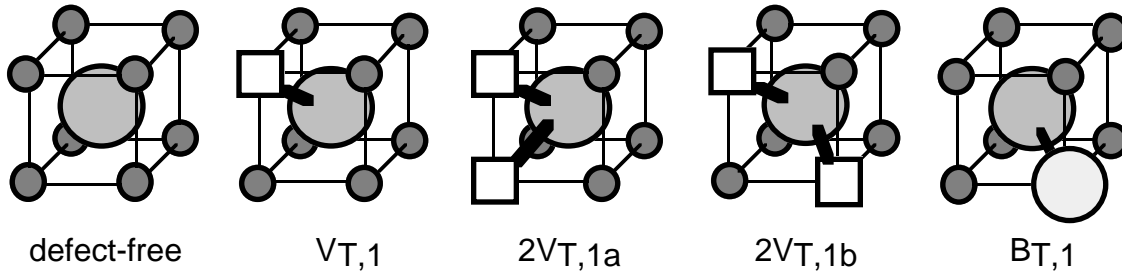
defects, because NiAl is of interest as a high-temperature structural material, and because point defects in annealed and quenched samples have already been extensively studied by PAC.

Previous PAC studies were carried out of point defects in annealed and quenched B2 (CsCl) compounds NiAl [3,4] and CoAl [4] and PdIn.[5,6,9] In these studies,  $^{111}\text{In}$  probes introduced into the alloys in high dilution (mole fractions  $\sim 10^{-8}$ ) are used to resolve their local atomic environments via the nuclear quadrupole interaction of the PAC level of the daughter  $^{111}\text{Cd}$  nucleus. The quadrupole interaction is a measure of the electric-field gradient (efg) induced by the defect, and is observed in the time domain as a “spin precession” of the PAC level. For the spin-5/2 PAC level of the  $^{111}\text{In}/\text{Cd}$  probe, the signal is a frequency-triplet labelled below by its fundamental precession frequency  $\omega_1$  and by the asymmetry parameter of the efg,  $\eta$ . [7] Because efg’s fall off with distance as  $r^{-3}$ , they are dominated by defects in the first few atomic shells, with distant defects only contributing to inhomogeneous broadening of the signals from closer defects. The PAC spectra consist of a superposition of signals, or perturbation functions, corresponding to ensembles of probe atoms having different local configurations of point defects near the probe atoms. The amplitudes of the perturbation functions correspond to the fractions of probes in each separate local configuration. The reader is referred to ref. [7] for further information about experimental methods and about the application of PAC to the study of point defects in metals and alloys.

For annealed samples of a generic B2 compound TB formed from a transition-metal (T) and trivalent metal (B), for example NiAl and PdIn, deviations from stoichiometry are accommodated with T-vacancies on the T-sublattice ( $V_T$ ) for T-deficient compositions and antisite T-atoms on the B-sublattice ( $T_B$ ) for T-rich compositions. For such “structural” defects, the concentration is determined by the deviation from stoichiometry. The In probe can be safely assumed to lie on the B-sublattice (that is,  $\text{In}_B$ ) in the aluminides because it is isovalent with Al, has a larger atomic radius than the (large) Al atom, and, finally, because  $\text{Al}_T$  antisite atoms are not observed as structural defects in these compounds and therefore must be high-energy elementary defects. For an  $\text{In}_B$  probe site, the four closest atomic shells belong to the T, B, B and T sublattices.

Analysis of PAC spectra of annealed and quenched NiAl,[3,4] CoAl [4] and PdIn [5,6,9] has led to identification of signals attributed to first-neighbor shell T-vacancies ( $V_{T,1}$ ), to two configurations of two first-neighbor T-vacancies ( $2V_{T,1a,b}$ ), to a T-antisite atom in the second-neighbor shell ( $T_{B,2}$ ), and to a combined configuration ( $V_{T,1} + T_{B,2}$ ). In addition, in PdIn, a signal observed in quenched samples was attributed to a 2nd or 3rd shell B-vacancy ( $V_{B,2}$  or  $V_{B,3}$ ), [6] and a high-frequency signal only observed in mechanically-milled samples has been attributed to a high-energy first-neighbor B-antisite atom ( $B_{T,1}$ ) considered to arise as a result of disordering between the two sublattices.[8] More recently, it has been shown from analysis of changes in defect concentrations due to a defect reaction that the signal for  $V_B$  is from shell 2 and not shell 3.[9] Relevant defect configurations are illustrated in Fig. 1, with quadrupole interaction parameters listed in Table 1.

In the present work, the site fractions of  $V_{\text{Pd},1}$  and  $\text{In}_{\text{Pd},1}$  measured after progressively longer milling times are used to determine the build-up in the vacancy concentration and lattice disordering. We shall assume below that defects are located at random in PdIn, so that the site fraction of the first-neighbor vacancy,  $f_V = f(V_{\text{Pd},1})$  should at first sight be expected to be given in terms of the vacancy concentration,  $c_V = c(V_{\text{Pd}})$  by the binomial probability  $f_V = 8c_V(1 - c_V)^7$ . However, since the separate interaction strengths for  $V_{\text{Pd},1}$  and  $\text{In}_{\text{Pd},1}$  are comparable, the combined presence of both defects would lead to a significantly different, and therefore unobserved, signal. Thus, the *observed* site fraction for  $V_{\text{Pd},1}$  corresponds to having one  $V_{\text{Pd}}$  defect and no  $\text{In}_{\text{Pd}}$  defects in the



**Figure 1.** Defect configurations in the first shell of In probes (large circle) in B2 compounds. The squares are T-metal vacancies and the mid-sized circle is a B-antisite atom.

**Table 1.** Quadrupole interaction parameters of relevant defect configurations in NiAl and PdIn.

Defect Configuration	NiAl		PdIn	
	$\omega_1$ (Mrad/s)	$\eta$	$\omega_1$ (Mrad/s)	$\eta$
defect-free	0	-	0	-
VT,1 first-shell T-vacancy	128	0	103	0
BT,1 first-shell B-antisite atom	-	-	67	~0.6
TB,2 second-shell T-antisite atom	19	~0	33	0
VB,2 second shell B-vacancy	-	-	~15	~0
2VT,1 (a) two VT in the first-shell (in	187	0.64	164	0.68
2VT,1 (b) two distinct configurations)	222	0.89	194	0.80

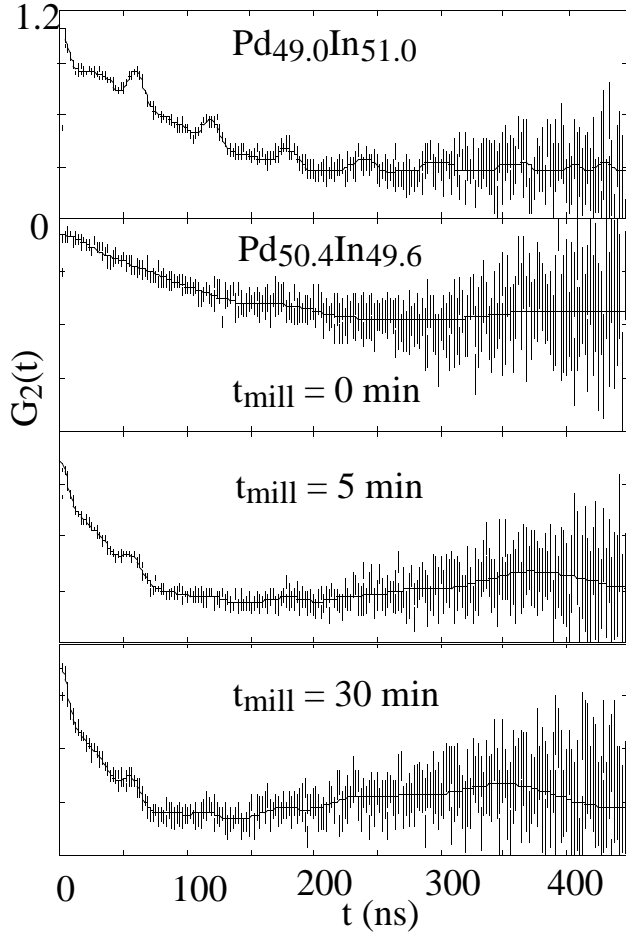
first neighbor shell, from which  $f_V = 8c_V(1-c_V)^7(1-c_A)^7$ . This expression was used in the analysis, together with the complementary expression  $f_A = 8c_A(1-c_A)^7(1-c_V)^7$  to determine  $c_A=c(\text{In}_{\text{Pd}})$  from measured values of  $f_A=f(\text{In}_{\text{Pd},1})$ .

## Experimental.

PdIn and NiAl samples containing trace amounts of  $^{111}\text{In}$  activity were prepared by arc-melting under argon. Weight losses during melting were small to negligible, and nominal compositions were taken to be the actual compositions. Samples were mechanically-milled under argon using a Spex 8000 vibrator mill. In the course of an earlier study of milled PdIn using a hardened steel vial,[8] chemical analysis revealed substantial contamination with Fe and Cr attributed to ablation of the surfaces of the vial and ball bearings. To reduce the possibility of such contamination in the present study, milling of PdIn was carried out using only WC vials and balls. X-ray analysis of one sample of milled PdIn revealed a nanocrystalline WC component, but appreciable alloying of the samples with W or C is not expected due to the extreme hardness of WC.

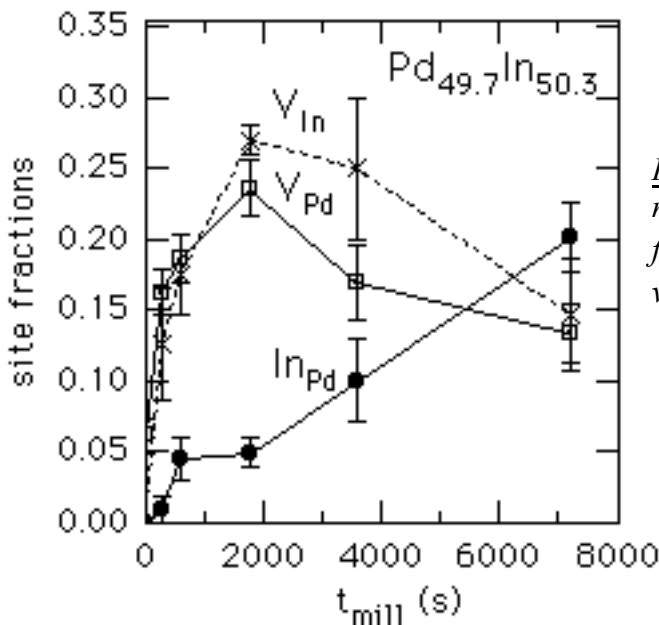
## Results for PdIn.

PAC spectra for PdIn were measured after milling for up to 2 hours, some of which are shown in Fig. 2. These spectra exhibit substantially less inhomogeneous broadening than those measured after milling in steel vials, [8] suggesting that sample contamination is sharply reduced. Spectra were fitted with superpositions of perturbation functions corresponding to the different defect configurations. Fitted site fractions for  $V_{\text{In},2}$ ,  $V_{\text{Pd},1}$  and  $\text{In}_{\text{Pd},1}$  are shown as a function of milling

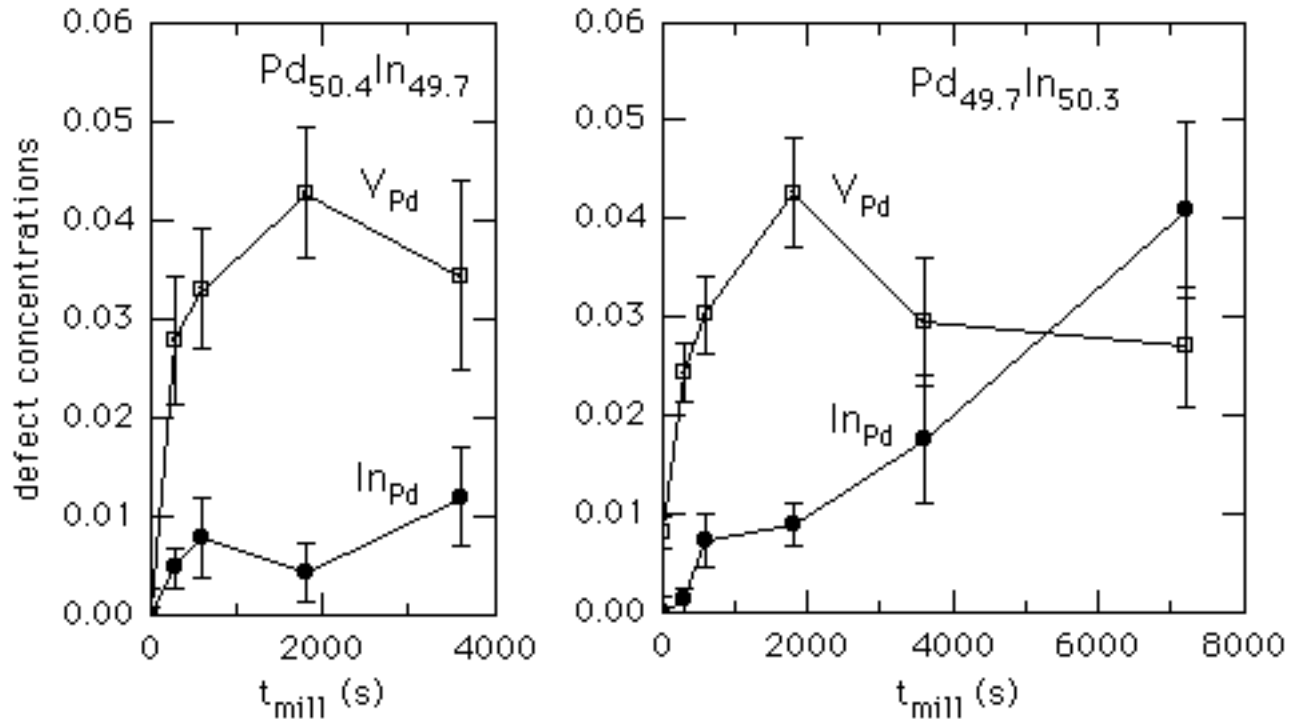


*Figure 2.* PAC spectra of PdIn. The top spectrum is of an annealed Pd-deficient sample, exhibiting a perturbation function with period  $\sim 60$  ns attributed to a Pd-vacancy next to the In probe atom. The bottom three spectra are of a Pd-rich sample, measured after annealing and after milling for 5 and 30 minutes. Spectra of the milled sample exhibit the perturbation function of the near-neighbor Pd-vacancy.

time for one of two samples in Fig. 3. As can be seen, site fractions for all three defects have increased significantly after the first 5 minutes of milling. The vacancy site-fractions each saturate at values of about 20% after milling for 10 minutes. Fig. 4 shows defect concentrations for  $V_{Pd}$  and  $In_{Pd}$  defects, derived from the site fractions by solving the equations given above for  $c_V$  and  $c_A$ , for



*Figure 3.* Site fractions of defect configurations near In probes in milled PdIn:  $V_{Pd}$  and  $In_{Pd}$  are first-shell defects while  $V_{In}$  is a second-shell vacancy.



*Figure 4. Concentrations of  $V_{\text{Pd}}$  and  $\text{In}_{\text{Pd}}$  defects in mechanically-milled samples of  $\text{Pd}_{50.4}\text{In}_{49.6}$  (left) and  $\text{Pd}_{49.7}\text{In}_{50.3}$  (right).*

samples having 49.7 and 50.4 at.% Pd. The vacancy concentration is observed to remain remarkably constant at a value of about 3.5(5)% after 5 minutes of milling, whereas, to a first approximation, the antisite atom concentration increases linearly with milling time, attaining a value of about 4% after 2 hours of milling.

### Results for NiAl.

PAC spectra for NiAl (not shown) were measured after milling a sample of NiAl with 50.5 at.% Ni in a hardened steel vial for 0-4 hours.[8,9] Site fractions were observed for the  $V_{\text{T},1}$  signal and  $2V_{\text{T},1}$  signals (summed together) which saturated after 10 minutes of milling at values of about 45% and 15%, respectively. The monovacancy site fraction is too large to be explained by a random distribution of Ni-vacancies, for which the maximum possible value is about 38%. The large site fractions are attributed to binding of Ni-vacancies to the impurity  $\text{In}_{\text{Al}}$  probes; the binding enthalpy has been measured elsewhere using PAC to be 0.22(1) eV.[4] While it is not possible to quantitatively extract a bulk vacancy concentration from these data, the magnitude of the site fractions suggests that, as for PdIn, the vacancy concentration is large and of the order of percents.

### Discussion.

Vacancy concentration in milled intermetallics. The vacancy concentration produced by milling of Pd-rich PdIn is about 3.5(5) at.%. Concerning differences between the two samples, it must be noted that the 49.7% Pd-poor sample should have 1.2% of structural Pd vacancies in the annealed state ( $4 \times 0.3\%$ ), so that the vacancy concentration added by milling is only about 2% instead of the 3.5% observed for the Pd-rich sample. This difference is not understood at this time, but might arise from differences in the hardness and/or slip mechanisms on the two sides of stoichiometry.

Enthalpy contribution from the vacancies. As shown in Fig. 3, the site fractions of  $V_{In,2}$  and  $V_{Pd,1}$  are comparable, leading to the conclusion that milling produces approximately equal numbers of vacancies on the two sublattices, that is, Schottky vacancy-pairs. The activation enthalpy for formation of the Schottky-pair was determined from PAC studies of quenched PdIn to be 1.3(2) eV.[6] This leads to an excess enthalpy contribution for 3.5% vacancies of about 4.4 kJ mol<sup>-1</sup>, comparable to measured enthalpies of the order of 10 kJ mol<sup>-1</sup>. Thus, at least for PdIn, vacancies are found to make a significant contribution to the total excess enthalpy.

Lattice disordering. The increase in antisite-atom concentration is attributed to progressive disordering between the two lattices. While the vacancy concentration was observed to build up rapidly during milling and to saturate at a level of several percent, the antisite-atom concentration appears to increase more gradually.

### Summary.

The method of perturbed angular correlation of gamma rays was applied to mechanically-milled intermetallic compounds to detect point defects and measure their concentrations. Large vacancy concentrations were observed in PdIn after milling for just a few minutes which were shown to have an associated excess enthalpy of about 4.4 kJ mol<sup>-1</sup>. The existence of such a large enthalpy contribution due to vacancies has not been commonly recognized heretofore, and may likewise form an important contribution to the excess enthalpy of other milled intermetallic compounds. Experiments are planned on other systems to determine the generality of the findings reached here primarily for PdIn.

### References.

- 
- \* Supported in part by the National Science Foundation under grant DMR 93-13702.
  - + E-mail address: collins@wsu.edu.
  - 1. H. Fecht, E. Hellstern, Z. Fu and W.L. Johnson, Adv. in Powder Metallurgy 1-3, 111(1989).
  - 2. C.C. Koch, J. of Non-Crystalline Solids, 117/118, 670 (1990).
  - 3. J. Fan and G. S. Collins, Hyperfine Interactions 60, 655 (1990).
  - 4. J. Fan, PhD Dissertation, Washington State University, 1992 (unpublished).
  - 5. H.-G. Müller and H. Hahn, Philosophical Magazine A50, 71 (1984).
  - 6. P. Sinha and G. S. Collins, Mat.Res.Soc.Symp.Proc. 364, 59 (1995).
  - 7. G. S. Collins, S. L. Shropshire and J. Fan, Hyperfine Interactions 62, 1 (1990).
  - 8. P. Sinha and G. S. Collins (submitted).
  - 9. Praveen Sinha, PhD Dissertation, Washington State University, 1995 (unpublished).