

A NEW APPROACH TO STUDY VACANCY DEFECTS IN HIGH-TEMPERATURE INTERMETALLIC COMPOUNDS

GARY S. COLLINS AND PRAVEEN SINHA

Washington State University, Department of Physics, Pullman, WA 99164

ABSTRACT

Perturbed angular correlations of gamma rays (PAC) is being applied to study defects in ordered intermetallic alloys. Vacancies on both Pd and In sublattices in the B2 system PdIn were detected after quenching through quadrupole interactions induced at nearby ^{111}In probe atoms. Fractions of probe atoms having each type of neighboring defect were observed to increase monotonically with quenching temperature over the range 825-1500 K. For compositions close to 50.15 at.% Pd, nearly equal site fractions were observed for Pd and In vacancies, indicating that the Schottky vacancy-pair defect is the thermal defect at high temperature. The formation enthalpy of the Schottky defect was determined to be 1.3(2) eV through analysis of quenching data from in the range 825-1200 K. Above 1200 K, however, the vacancy concentration was observed to saturate at a value of 1.4(2) atomic percent, perhaps due to breakdown of the law of mass action for high defect concentrations.

INTRODUCTION

Thermally-activated point defects may play an important role in the mechanical properties of ordered alloys at high temperature. To determine properties and concentrations of the point defects in such alloys, we have been applying the technique of perturbed angular correlations of gamma rays (PAC).[1] The defects are observed through quadrupole interactions induced at nuclei of neighboring probe atoms. In metals, where interaction strengths fall off as one over the distance cubed between defect and probe, signals are dominated by different configurations of defects within the first few atomic shells around the probes. Using the sensitive ^{111}In probe, such signals have been resolved and identified with the underlying configurations. Signal amplitudes of fitted PAC perturbation functions equal the site fractions of probes in each corresponding local environment. For further information about PAC and its use to study point defects, the reader is referred to ref. [1].

Initial studies were made on B2-phase alloys such as NiAl,[2,3,4] CoAl,[3,4] and PdIn.[5] The B2 phases of these alloys extend over wide ranges of composition, and accommodate deviations from stoichiometry with structural point defects: transition-metal vacancies (e.g., V_{Pd}) and transition-metal antisite atoms (e.g., Pd_{In}), respectively, for compositions poor and rich in the transition metal. Samples were prepared by arc-melting high-purity elements together with carrier-free ^{111}In (mole fraction at the part-per-billion level). To identify the defects, measurements on samples processed so as to enhance concentrations of selected defects were analysed: (1) *annealing* yields equilibrium structural defects,[2,4,5] (2)

quenching exhibits thermally-activated defects;[3,4,5] (3) *mechanical milling* generates high-energy defects by plastic deformation.[5] In studies on NiAl, for example, signals have been identified with various defect configurations near In_{Al} probes: one V_{Ni} in the first-neighbor atomic shell, two distinct configurations of two V_{Ni} 's in the first shell, one Ni_{Al} antisite atom in the second shell, and the combination of a V_{Ni} in shell 1 and a Ni_{Al} in shell 2. For NiAl and CoAl, measurements made on quenched samples have shown that the thermal defect is the Schottky vacancy-pair.[6] Formation enthalpies, E_{F} , and entropies, S_{F} , have been determined through analysis of the temperature dependence of quenched-in site fractions using a methodology developed at WSU.[6] For NiAl, the value $E_{\text{F}}= 2.22(8)$ eV was obtained.[6]

NiAl(^{111}In) and CoAl(^{111}In) have impurity probes and, as a result, site fractions of first-shell vacancies are enhanced by an attractive interaction between vacancy and probe, with binding enthalpies of about 0.20 eV [4]. PdIn(^{111}In), on the other hand, is a non-impurity system, so that site fractions can be directly related to defect concentrations if, as assumed below, the defects are located at random. Recently,[5] we identified PAC perturbation signals for eight defect configurations in PdIn. These include signals for one V_{Pd} defect in the first shell of the In probe,[7] with quadrupole coupling frequency $\omega_1= 103$ Mrad/s and electric-field gradient asymmetry parameter $\eta\sim 0$, and for one V_{In} defect in either the second or third shell, with $\omega_1= 17$ Mrad/s and $\eta\sim 0$. V_{Pd} was identified from observations that it is prominent in annealed Pd-poor alloys, quenched alloys, and milled alloys. V_{In} was identified by the process of elimination after being observed after quenching. For further details, see ref. [5].

In the present work, we present a quantitative analysis of measurements on quenched PdIn samples for compositions very close to stoichiometry, 50.15(10) at.% Pd. Hahn and Mueller previously studied PdIn using PAC,[7] but their work was restricted to a smaller range of quenching temperature, the signal of the V_{In} defect had not been identified, and they did not determine a formation enthalpy. Elsewhere, measurements will be reported on quenched samples with greater Pd concentrations.

EXPERIMENTS

High-purity Pd and In metals were arc-melted together with carrier-free ^{111}In (mole fraction $\sim 10^{-8}$) and annealed. Samples were quenched after equilibrating them at temperatures, T_{q} , between 825 and 1500 K for 1 hour in a vertical tube furnace by dropping them into a water bath. All annealing and quenching was carried out with samples wrapped tightly in Ta foils to reduce changes in composition due to evaporation of In. Nominal compositions were obtained from weights prior to melting after adjustment for slight losses during annealing or quenching attributed to In evaporation. The quenching rate was estimated to be about 10^4 K/sec.[4] PAC measurements were made at room temperature using a spectrometer and methods described elsewhere.[1]

Fig. 1 exhibits PAC spectra for samples near 50.15% Pd after annealing (top) and after quenching from 1148 K (middle) and 1373 K (bottom). The signal for In probes with a V_{Pd} defect in the first neighbor shell is visible as “peaks” with a periodicity of 60 ns in the spectra measured after quenching. Less clearly visible but unambiguously present in the computer fits is the V_{In} signal, with period 370 ns, as well as other signals.[5] The amplitude of the V_{Pd} signal (equal to the site fraction of In probes next to a V_{Pd} defect) increases with quenching temperature as expected for a thermal defect.

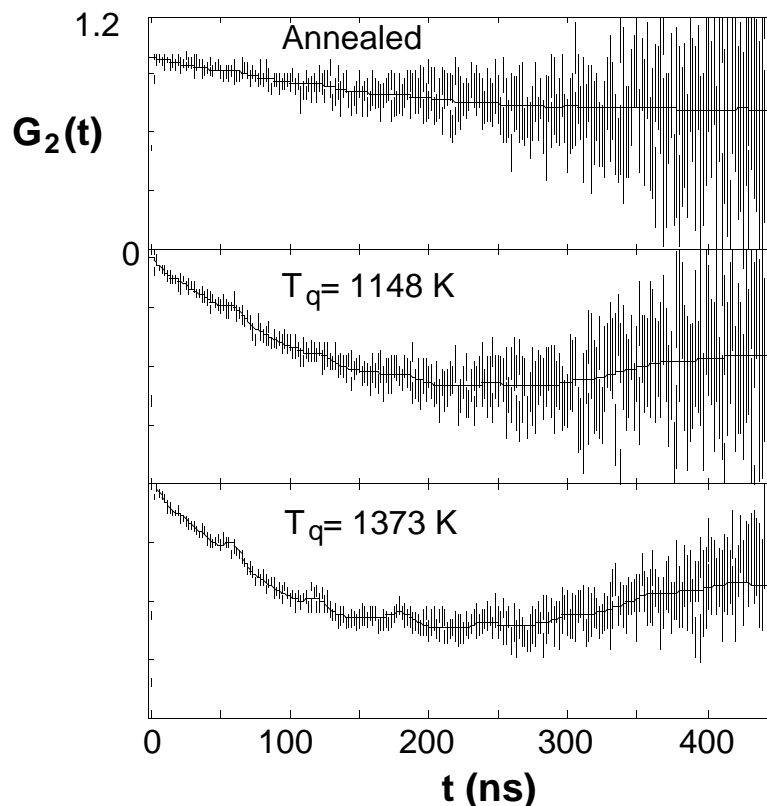


Fig. 1. PAC spectra of PdIn measured after annealing or quenching from the indicated temperatures. Quenched spectra exhibit signals near In probe atoms due to Pd vacancies (60 ns period) and In vacancies (370 ns period).

In Fig. 2 are shown the fitted site fractions for V_{Pd} (top) and V_{In} (bottom) as a function of quenching temperature. The solid curve is from a computer fit described below. Qualitatively, the vacancy site fractions $f(V_{Pd})$ and $f(V_{In})$ increase with T_q up to about 1200 K and saturate thereafter. Assuming that the elementary point defects which constitute the thermal defect are located at random, then the site fraction $f(V_{Pd})$ of first-shell V_{Pd} defects is related to the vacancy concentration $c=[V_{Pd}]$ by the familiar binomial expression $f(V_{Pd})= 8c (1-c)^7$. For $T_q > 1300$ K, the average value of $f(V_{Pd})$ is 10(1)%, from which is obtained the concentration $c= 1.2(1)\%$.

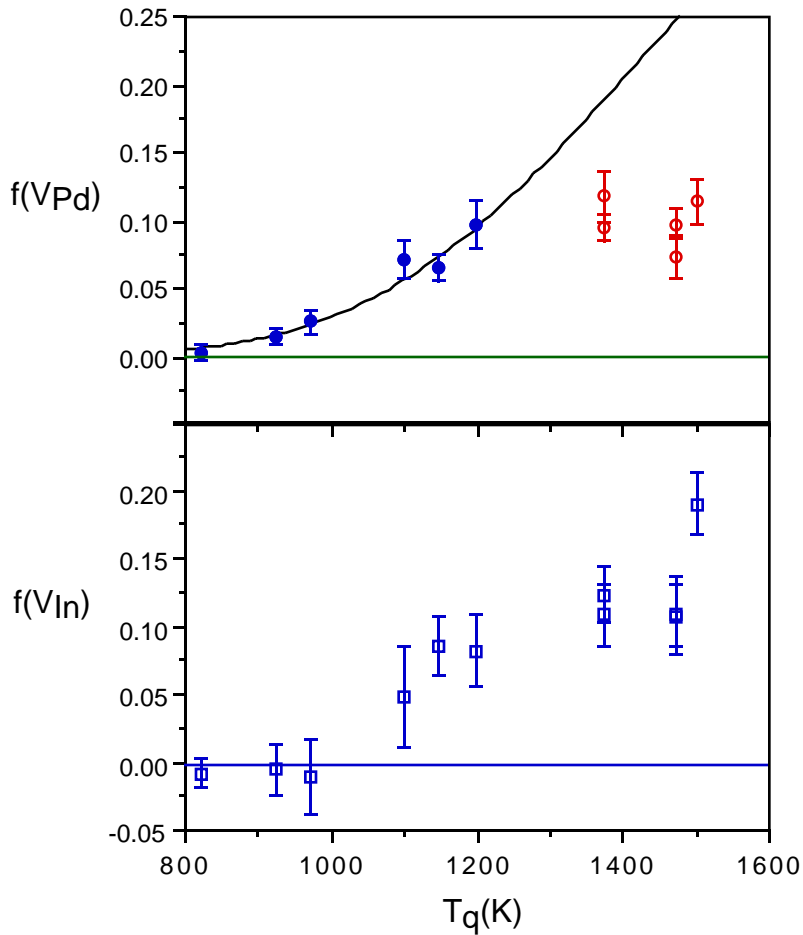


Fig. 2. Site fractions of In probe atoms in PdIn having near-neighbor vacancies on the Pd sublattice (top) or nearby vacancies on the In sublattice (bottom), measured after quenching from the temperatures indicated. The drawn curve at top is the result of a fit of the concentration of Pd-vacancies corresponding to the filled points to an Arrhenius temperature dependence.

RESULTS

What is the thermal defect in PdIn? For PdIn to remain a single B2-phase alloy at high temperature, as shown in its phase diagram, the thermal defect must conserve the lattice. This means that the defect is formed by transformation of whole molecules of the solid. The two most likely candidates are the *Schottky defect*, formed by removing a molecule to the surface, leaving behind a vacancy on each sublattice, $0 \rightarrow V_{Pd} + V_{In}$, and the *triple defect*, which can be thought of as forming out of a Schottky defect by transfer of a neighboring Pd_{Pd} atom to the In vacancy: $V_{Pd} + V_{In} + Pd_{Pd} \rightarrow 2V_{Pd} + Pd_{In}$. For the triple defect, $2V_{Pd} + Pd_{In}$, (or its complement, $2V_{In} + In_{Pd}$) vacancy defects should only be observed on one sublattice. However, Fig. 2 shows that site fractions for V_{Pd} and V_{In} are nearly equal over the entire temperature range, from which it is concluded that the thermal defect is the Schottky defect and not a triple defect.

Schottky defect properties can be obtained as follows. Assuming strictly equal numbers of V_{Pd} and V_{In} defects and that the law of mass action applies, defect concentrations are given in terms of the activation enthalpy and entropy of formation, E_F and S_F respectively, of the Schottky defect by

$$[V_{Pd}] = [V_{In}] = \exp(S_F/2k_B) \exp(-E_F/2k_B T). \quad (1)$$

Concentrations $c = [V_{Pd}]$ were obtained from $f(V_{Pd})$ using the binomial expression given above and then fitted with eq. 1. Derived values of c are plotted in Fig. 3 in the form $\ln(c)$ versus T^{-1} . Data from temperatures above $T_q = 1300$ K that exhibit saturation which is inconsistent with eq. 1 were excluded from the fit. The six data at lower temperature (filled circles) are observed to follow the expected Arrhenius behavior. A fit of those data to eq.

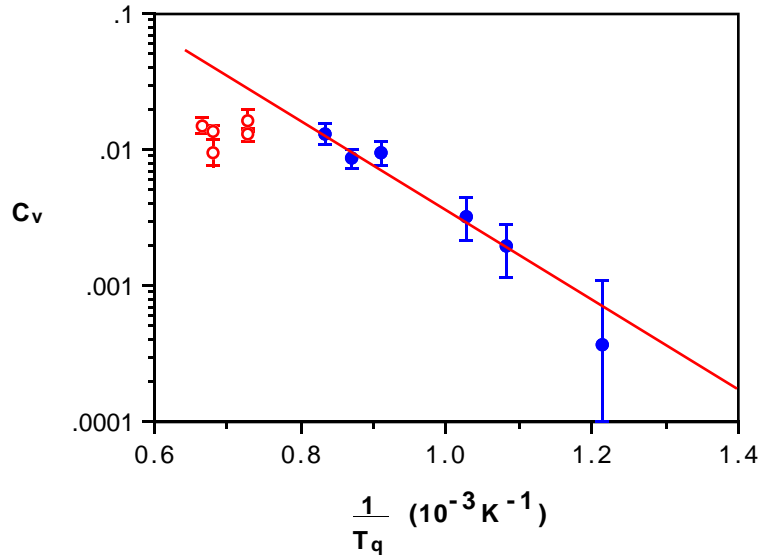


Fig. 3. Logarithm of the Pd-vacancy concentration in PdIn versus the reciprocal of the quenching temperature. The drawn curve is from a fit of the data with filled circles to eq. 1.

1 is shown by the drawn curves in Fig. 2 and 3, yielding $\exp(S_F/2k_B) = 7.2(6.7)$, or $S_F \sim 4k_B$, and $E_F = 1.30(18)$ eV. These values are in satisfactory agreement with other indications: The value of S_F is close to what one calculates for two isolated vacancies using an Einstein lattice-vibrational model. Dilatometric measurements [8] of c analysed assuming a Schottky defect model yielded two different values of E_F whose average is 1.47 eV in the range of our fit. Defect concentrations obtained from the dilatometric measurements are in excellent agreement with our measurements for T_q less than 1000 K but fall 30% below our measurements for $1000 \text{ K} < T_q < 1273 \text{ K}$. Alternatively, because sites of one sublattice of the B2 structure are surrounded by sites of the other, the activation enthalpy may also be crudely estimated from the sum of enthalpies of formation of vacancies in the pure metals of the constituent elements; for PdIn this yields 1.95 eV.[9]

Saturation of defect concentrations for $T_q > 1300 \text{ K}$ is not anticipated using eq. 1. One possible explanation is that vacancies anneal out or cluster during quenching from high temperatures. We believe that this is not the case based on the lack of any observed tendency toward defect saturation in studies of NiAl and CoAl quenched from temperatures as high as 1673 K.[3,4] A second hypothesis is that the law of mass action used to derive eq. 1 breaks down when vacancy concentrations exceed 1%, as they do here above 1300 K. The law applies rigorously only for low concentrations of non-interacting defects.

To summarize, we applied the technique of perturbed angular correlations of gamma rays (PAC) to study thermal defects in the ordered alloy PdIn. Pd and In vacancies were separately monitored in measurements on quenched, Pd-rich samples and their presence in roughly equal concentrations is consistent with the thermal defect at high temperature being the Schottky vacancy-pair and not the triple-defect. Arrhenius behavior of the quenched-in vacancy concentration was analysed using the law of mass action to obtain the enthalpy and entropy of formation of the Schottky defect pair. Quenching from temperatures in excess of 1300 K leads to saturation of vacancy concentrations which is considered to reflect breakdown of the law of mass action.

ACKNOWLEDGMENT

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1. G.S. Collins, S.L. Shropshire and J. Fan, *Hyperfine Interact.* **62**, 1 (1992).
 2. Jiawen Fan and Gary S. Collins, *Hyperfine Interactions* **60**, 655 (1990).
 3. Gary S. Collins and Jiawen Fan, *Hyperfine Interactions* **80**, 1257 (1993).
 4. Jiawen Fan, PhD dissertation, Washington State University, 1992.
 5. Praveen Sinha and Gary S. Collins (submitted).
 6. Gary S. Collins and Jiawen Fan (submitted).
 7. H. Hahn and H.-G. Mueller, *Phil. Mag.* **A50**, 71 (1984).
 8. W. Puff, A.G. Barogh and H. Wever, *Mat.Sci. Forum* **105-110**, 1181 (1992).
 9. H. Bakker, *Mat. Sci. Forum* **15-18**, 1155 (1987).