

Vacancy-Vacancy Interactions in NiAl

Matthew O. Zacate and Gary S. Collins

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

Keywords: point defect, vacancy, defect interaction, intermetallic compound, perturbed angular correlation, PAC, NiAl

Abstract. Interactions between Ni vacancies in Ni-poor NiAl were investigated using the method of perturbed angular correlation of gamma rays. Measurements were made at temperatures up to 1050 °C on samples in the composition range 49.0 to 49.8 at.% Ni, for which there is a fixed concentration of structural Ni vacancies. Site fractions of complexes of vacancies with In solute atoms were determined from amplitudes of quadrupole interaction signals. The binding energy between a vacancy and In solute was determined to be 0.154(7) eV from fits of site-fraction ratios. Binding energies of a second vacancy in three distinct configurations were determined in the same way to be 0.086(10), 0.154(6) and 0.135(14) eV, respectively, for vacancies in first-, second- and third-neighbor positions on their own sublattice. Estimates of the vacancy-vacancy interaction energy are obtained from differences between binding energies of the first and second vacancies, and found to be 0.068, 0.000, and 0.019 eV for the corresponding positions. Thus, vacancies are repelled from first-neighbor positions and favor second-neighbor positions slightly. Overall, the interaction energies are found to be relatively small.

Introduction

Interactions among point defects are often neglected in the analysis of diffusion measurements. Little is known experimentally about such interactions. Particularly for nonstoichiometric phases in which point defect concentrations can be extremely high, the interactions may have an appreciable effect on diffusion. The present measurements were undertaken to determine how vacancies interact in NiAl, a high-temperature structural material that has the CsCl structure and a phase field extending from 45-60 at.% Ni.

Measurements were made to detect vacancies on the Ni-sublattice using perturbed angular correlation of gamma rays (PAC). The probe is an In solute atom which in the perfect crystal sits on the Al-sublattice with eight Ni-atoms in the first neighbor shell. Ni-vacancies in the first shell produce large electric-field-gradients (efg's) that are sensed through interaction with the nuclear quadrupole moment of the probe atom. The interaction for a specific configuration of vacancies is characterized by a quadrupole interaction frequency ω_1 and efg asymmetry parameter η . ω_1 is the fundamental observed frequency and $\eta=0$ when there is a three-fold or higher axis of charge symmetry. For further information about the application of PAC in defect studies, see ref. [1]. Six possible configurations of vacancies with In-probe atoms are shown in Fig. 1, including in particular three inequivalent double-vacancy (2V) configurations. Also shown in the figure are interaction frequencies, normalized to the monovacancy (1V) frequency, and asymmetry parameters determined from calculations of efg's in the point-charge approximation.

Measurements were made on four samples of $\text{Ni}_{1+2x}\text{Al}_{1-2x}$ with compositions in the range 49.02 to 49.78 at.% Ni between room temperature and 1050 °C. For that range of composition and temperature, the alloys are single-phase and have the CsCl structure. The concentration of structural vacancies on the Ni-sublattice can be expressed in terms of the deviation from stoichiometry, x , as $[V] = -4x/(1 - 2x)$, and the thermal vacancy concentration is much smaller.

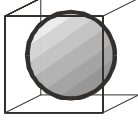
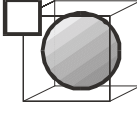
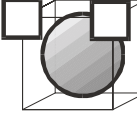
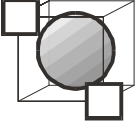
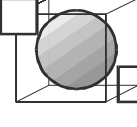
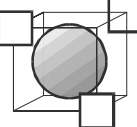
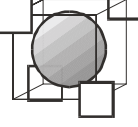
						
0V	1V	2Va	2Vb	2Vc	3Vc	4V
$\omega_l=0$	$\omega_l=1, \eta=0$	$\omega_l=1.7, \eta=1$	$\omega_l=1.7, \eta=1$	$\omega_l=2, \eta=0$	$\omega_l=1, \eta=0$	$\omega_l=0$

Fig. 1. Structures of vacancy-probe complexes in NiAl.

When In probes have different numbers of vacancies the first neighbor shell, the PAC spectrum will be a superposition of signals for configurations such as shown in Fig. 1. The amplitude of a signal is equal to the fractional number of probes in that arrangement, called the site-fraction. Vacancies have an attractive interaction with In probes. In thermal equilibrium, it can be shown that the ratio of site fractions of the 1V-complex to the defect-free, 0V-site is given in terms of the vacancy concentration [V] and binding energy E_{B1} of the first vacancy to the probe by

$$\frac{f_1}{f_0} = 8[V]\exp(E_{B1} / k_B T). \quad (1)$$

In eq. 1, a binding-entropy factor was set to unity. A positive value of E_{B1} indicates an attractive interaction. Ratios of site fractions of 2V-sites to the 1V-site are given by similar equations:

$$\begin{aligned} \frac{f_{2a}}{f_1} &= \frac{3}{2}[V]\exp(E_{B2a} / k_B T), \\ \frac{f_{2b}}{f_1} &= \frac{3}{2}[V]\exp(E_{B2b} / k_B T), \text{ and} \\ \frac{f_{2c}}{f_1} &= \frac{1}{2}[V]\exp(E_{B2c} / k_B T), \end{aligned} \quad (2)$$

in which E_{B2a} , E_{B2b} , and E_{B2c} are binding energies of a second vacancy to a 1V-complex in configurations 2Va, 2Vb and 2Vc. The prefactors equal the numbers of equivalent ways in which 2V-complexes can be formed (i.e., 12, 12, and 4, respectively) divided by the number of ways in which a 1V-complex can be formed (i.e., 8).

PAC offers the possibility of observing vacancy-vacancy interactions in several ways. For example, a strong vacancy-vacancy attraction would lead to clustering and therefore reduce the number of vacancies that could trap next to probe atoms. In this situation, [V] in eqs. 1 and 2 would represent a ‘free’ vacancy concentration that is close to the total vacancy concentration $[V] = -4x/(1-2x)$ at high temperature but reduced at low temperature. A strong vacancy-vacancy repulsion would increase the site fraction of 1V-sites relative to 2V-sites. In the absence of vacancy-vacancy interaction and lattice relaxation, the three 2V binding energies $E_{B2a,b,c}$ are equal. A vacancy-vacancy interaction that depends on the distance separating vacancies will lead to differences in 2V binding energies. For example, a stronger attraction between vacancies in second neighbor positions on their sublattice would make E_{B2b} more positive than E_{B2a} or E_{B2c} .

Experiment

Four 100-mg samples of NiAl were prepared by arc melting 5N metal foils with carrier-free ^{111}In under Ar. The fractional concentration of indium was about 10^{-8} . Samples were annealed at 1050 °C under H_2 for one hour. Compositions were determined from masses of the foils before arc-melting. Minor mass loss during the melting process is considered in the quoted uncertainties in composition. PAC measurements were made at temperatures up to 1050°C using a spectrometer [1] with four BaF_2 detectors at angles of 90°. Site-fractions of the quadrupole interaction signals were obtained by fitting spectra with superpositions of perturbation functions.

Hyperfine interaction signals and identifications with vacancy complexes

Hyperfine parameters of signals observed and their attributions are listed in Table 1. The 0V, 1V, 2Va and 2Vb signals were reported in previous work [2-4]. Typical PAC spectra measured at 300 °C in the present work are shown in Fig. 2. Time-domain spectra are shown on the left and fourier amplitudes on the right. For the sample with 49.75(3) at.% Ni, close to stoichiometry, a signal with $\omega_1=128$ Mrad/s dominates (Fig. 2 top) that has been attributed to the 1V-complex [2]. The signal has a 1:2:3 ratio of frequencies, indicating that $\eta=0$. The same signal is prominent in Ni-rich samples after quenching [3] or measuring at high temperature [4]. The spectrum for the 49.51(5) at.% Ni sample (Fig. 2 bottom) exhibits more clearly a signal with $\omega_1=187$ Mrad/s that has been attributed to a 2V-complex [2] and is attributed as described below to vacancies in the 2Vb configuration. The frequency ratios here are not harmonic, indicating that $\eta \neq 0$. Also present and fitted in these and other spectra are signals with $\omega_1=224$, 208 and 143 Mrad/s and attributions given in Table 1.

Vacancy configuration	ω_1 [Mrad/s]	η
0V	~ 0	0
1V	128.1(2)	0
2Va	224(2)	0.84(3)
2Vb	187.2(6)	0.65(2)
2Vc	208(5)	0
3V	143(3)	0.15(3)
4V	~ 0	0

Table 1. Hyperfine interactions at room temperature and site identifications.

Observed variations of site fractions with temperature and composition suggest that the 187, 224 and 208 Mrad/s signals are from the three 2V-complexes shown in Fig. 1. Corroboration comes from point-charge calculations of efg's in the absence of lattice relaxation. Complexes 2Va and 2Vb have been observed in other intermetallics having the CsCl structure [5]. Matching the 224 and 187 Mrad/s signals (with nonzero η) with the 2Va and 2Vb configurations requires additional information. The experimental inequality of frequency and asymmetry parameter for 2Va and 2Vb configurations is attributed to lattice relaxation. The site-fraction of the 187 Mrad/s signal is always observed to be greater than the site-fraction of the 224 Mrad/s signal, although they should be the same if vacancies were located at random in the first neighbor-shell of probe atoms. Diffuse x-ray scattering has been reported to show that vacancies in Ni-poor NiAl avoid near-neighbor positions on their own sublattice [6]. Considering the structures of 2Va and 2Vb

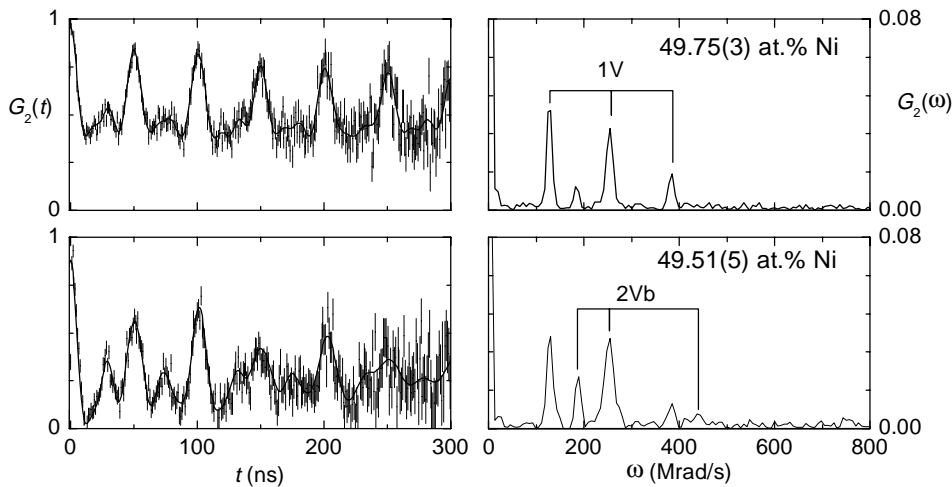


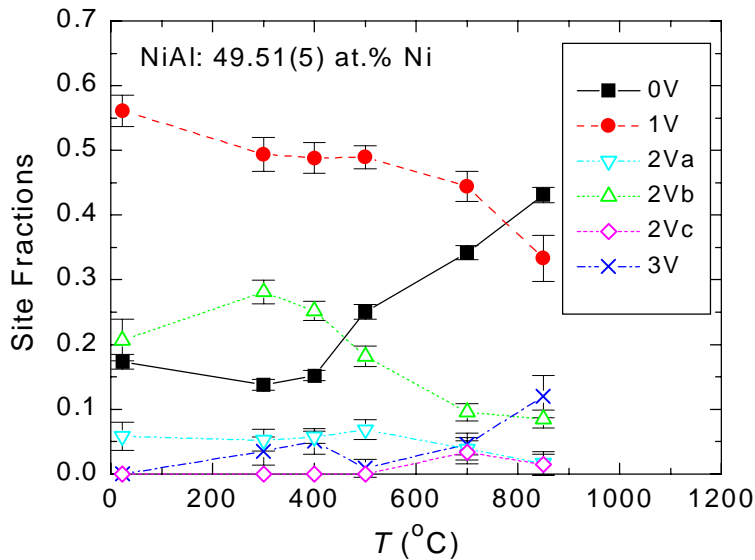
Fig. 2. PAC spectra of NiAl measured at 300 °C.

in light of that idea, the 187-Mrad/s signal is assigned to configuration 2Vb. (Given these new assignments, opposite assignments that were made for configurations 2Va and 2Vb in previous papers, e.g. [5], were incorrect.) The 143 Mrad/s signal is attributed with less certainty either to the 3V-complex shown in Fig. 1 or to a complex of two Ni-vacancies, one in each of neighbor shells one and four. An even higher-order complex is the 4V-complex shown in Fig. 1, with hyperfine interactions indistinguishable from the defect-free, 0V site. It is more likely to be observed at low temperature and for the 49.0 and 49.5 at.% alloys that have higher concentrations of structural vacancies.

Determination of binding energies

Temperature dependences of site-fractions for the 49.51 at.%Ni sample are shown in Fig. 3, and are representative of data for the other three samples. With increasing temperature, site fractions of vacancy complexes decrease, with an increase in the defect-free site-fraction (0V).

Ratios of site fractions were analyzed according to eqs. 1 and 2 for the four samples. When site-fraction ratios are divided by the vacancy concentration and by the prefactors in eqs. 1 and 2, one obtains *binding enhancement factors* $\exp(E_B/k_B T)$. In Fig. 4 are shown Arrhenius plots of binding enhancement factors at the four highest temperatures for the 49.51 at.% sample. (The two low temperature measurements were excluded from analysis because they were either not in equilibrium (20 °C) or were believed to be disturbed by the presence of 4V complexes with cubic



symmetry that have a zero-frequency interaction indistinguishable from the 0V signal.) The enhancement factors were fitted to obtain the binding energies, with results shown in the figure. (For clarity, enhancement factors for configuration 2Vc are not shown). Binding energies obtained from such analysis for all four samples are tabulated in Table 2, with unweighted averages in the bottom row.

Fig. 3. Site fractions of vacancy configurations in NiAl.

Sample Composition [at.% Ni]	E_{B1} [eV]	E_{B2a} [eV]	E_{B2b} [eV]	E_{B2c} [eV]
49.02(5)	0.152(3)	0.06(2)	0.152(3)	0.11(1)
49.51(5)	0.172(2)	0.086(8)	0.167(5)	0.16(1)
49.75(3)	0.136(3)	0.088(2)	0.14(1)	0.16(5)
49.78(5)	0.156(3)	0.11(1)	0.156(3)	~0.1
average	0.154(7)	0.086(10)	0.154(6)	0.135(14)

Table 2. Binding energies between vacancies and In solutes

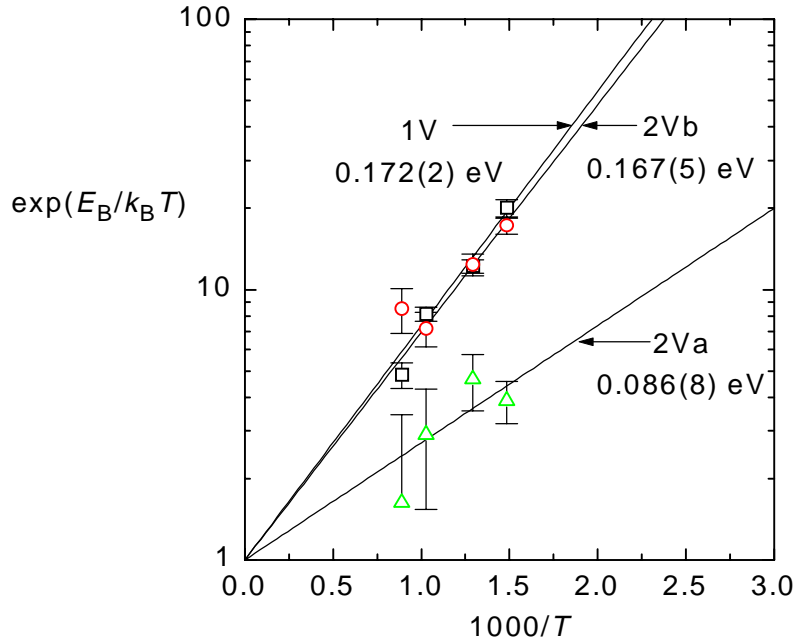


Fig. 4. Binding enhancement factors for vacancy complexes. Shown are site-fraction ratios divided by total vacancy concentration $[V]$ and prefactors in eqs. 1 and 2. Symbols: 1V, squares; 2Va, triangles; 2Vb, circles. Factors for complex 2Vc are not shown for clarity.

Examination of binding enhancement factors did not show convincing evidence of curvature as would occur if there were a strong vacancy-vacancy attraction. Some enhancement factor data derived from the ratio f_1/f_0 exhibited negative curvature at low temperature. For the data in question, the 3V site fraction was large and there is an open question as to the presence of 4V complexes (see Fig. 1). Since the probe in a 4V-complex is a position with cubic point symmetry, the interaction frequency is zero and therefore 4V-complexes cannot be distinguished from defect-free probes (0V). Such data were excluded in the analysis.

Discussion

Table 2 shows significant differences among binding energies of the vacancies. Whereas E_{B1} and E_{B2b} are equal to 0.154 eV, E_{B2a} is much smaller at 0.086 eV and E_{B2c} has an intermediate value of 0.135 eV. The question arises whether these differences are solely caused by vacancy-vacancy interactions that vary with the distance between vacancies or are disturbed by the presence of the In probe atom. The close equality between binding energies E_{B1} and E_{B2b} suggests that the presence of the probe does not disturb the relative energies of interaction of vacancies in the different configurations. Therefore, the reduced binding energy of the second vacancy in configuration 2Va is attributed to repulsion between vacancies in first-neighbor positions on their own (simple cubic) sublattice. Under these assumptions, the magnitude of the repulsive interaction energy is $(0.154 - 0.086) = 0.068(12)$ eV for vacancies in first-neighbor positions, and 0.000(10) and 0.019(16) eV in second- and third-neighbor positions.

The interaction energies are plotted in Fig. 5, where it can be seen that the second-neighbor configuration of vacancies has the lowest energy. This is consistent with the observed tendency for vacancies in Ni-poor NiAl to avoid first-neighbor sites [6] and, with increasing deviation from stoichiometry, to aggregate on 111 planes ultimately leading to a phase transformation to the Ni_2Al_3 phase [7]. A tendency for Ni-vacancies to cluster in first-neighbor positions would of course lead to phase separation of Ni and Al. The interaction energies obtained are in reasonably good agreement with results of a recent calculation of interaction energies [8], shown by the dashed line in Fig. 5.

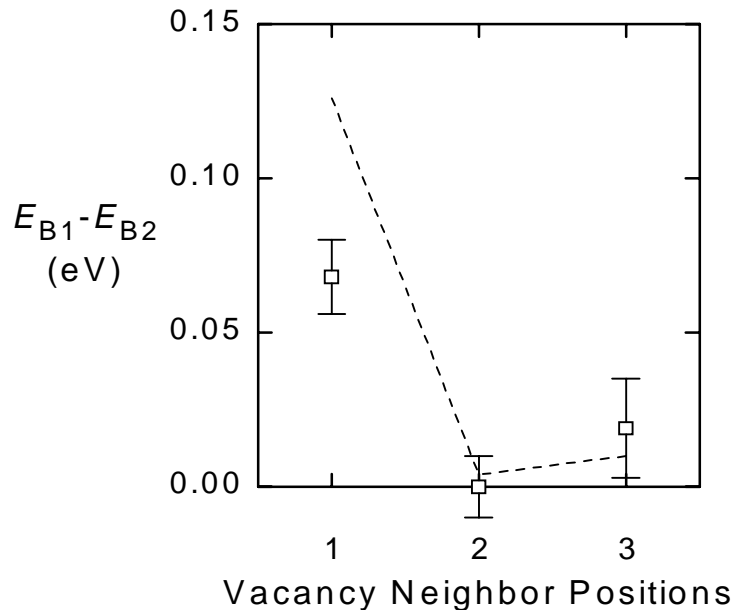


Fig. 5. Vacancy-vacancy interaction energies for Ni-vacancy pairs in first, second and third neighbor positions on the Ni-sublattice. The dashed line shows calculations from ref. [8].

In summary, PAC measurements were carried out on Ni-poor NiAl to study vacancy-vacancy interactions. Principal findings are binding energies of Ni-vacancies to In-probe atoms in several distinct configurations. Equality between binding energies of the first vacancy and a second vacancy in the 2Vb configuration is taken to indicate that lattice relaxations around indium impurity probe atoms do not significantly modify the binding energies. Differences between binding energies of the first vacancy and of second vacancies in configurations in which the vacancies are separated by first-, second-, and third-neighbor distances are taken to represent the probe-free interaction energies. These are repulsive for vacancies in first-neighbor positions and neutral for vacancies at greater distances. Such a repulsive near-neighbor interaction is of course necessary to avoid phase separation.

Acknowledgement

This work was supported in part by the National Science Foundation under grant DMR 96-12306 (Metals Program).

References

- [1] G. S. Collins, S. L. Shropshire and J. Fan, *Hyperfine Interactions* Vol. 62 (1990) pp. 1ff.
- [2] J. Fan and G. S. Collins, *Hyperfine Interactions* Vol. 60 (1990) pp. 60ff.
- [3] Gary S. Collins, Jiawen Fan and Bin Bai, in *Structural Intermetallics 1997*, eds. M.V. Nathal et al. (The Minerals, Metals and Materials Society, 1997), pp. 43ff.
- [4] Bin Bai and Gary S. Collins, in *High-temperature ordered intermetallic alloys VIII*, eds. E.P. George, M. Mills and M. Yamaguchi, Materials Research Society Symposium Proceedings Vol. 552 (1999) pp. 541ff.
- [5] Gary S. Collins, Praveen Sinha and Mingzhong Wei, *Hyperfine Interactions* Vol. (C)1 (1996) pp. 380ff.
- [6] P. Georgopoulos and J.B. Cohen, *Acta. Met.* Vol. 29 (1981) pp. 1535ff.
- [7] G.W. West, *Phil. Mag.* Vol. 9 (1964) pp. 979ff.
- [8] P.A. Korzhavyi et al., *Phys. Rev. B* Vol. 61 (2000) pp.6003ff.