

## Thermal Defects in B2 Iron Aluminide

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### ABSTRACT

Thermal defects in B2 FeAl samples with compositions between 49.5 and 54.7 at.% Fe were investigated using perturbed angular correlation of gamma rays (PAC). Vacancies on the Fe-sublattice were detected through quadrupole interactions induced at adjacent  $^{111}\text{In}/\text{Cd}$  probe atoms on the Al-sublattice. Five high-frequency quadrupole-interaction signals were detected (greater than 50 Mrad/s) that are attributed to complexes involving 1, 2, 3, 4 and (with less certainty) 5 Fe-vacancies in the first neighbor shells of the probes. These attributions are based on (1) a comparison between measured quadrupole interaction parameters and point-charge calculations of electric-field gradients for possible vacancy-probe complexes; and (2) numerical simulation of the evolution of site fractions of probes in the complexes at lower temperatures. Measurements were made at temperatures up to 950 °C. Assuming that the equilibrium high-temperature is the triple defect (2 Fe-vacancies and one Fe-antisite atom), measurements over the range 600-900 °C yield a formation enthalpy of 1.1(1) eV for the triple defect. Below about 600 °C, Fe-vacancies are quenched-in with a fractional concentration of the order of 1 at.% close to stoichiometry. However, quenched-in vacancies continue to jump over short distances and trap next to the impurity probes atoms in day-long measurements down to 200 °C. Simulations of site fractions below 700 °C were used to determine binding enthalpies of vacancies with probe complexes. Binding enthalpies obtained for the first four vacancies were 0.23, 0.23, 0.15 and 0.18 eV. Simulations in the range 200-700 °C suggest a negative value for the formation entropy. The negative value indicates either that triple defects stiffen the B2 lattice or that repulsive defect-defect interactions become important at the high defect concentrations in FeAl.

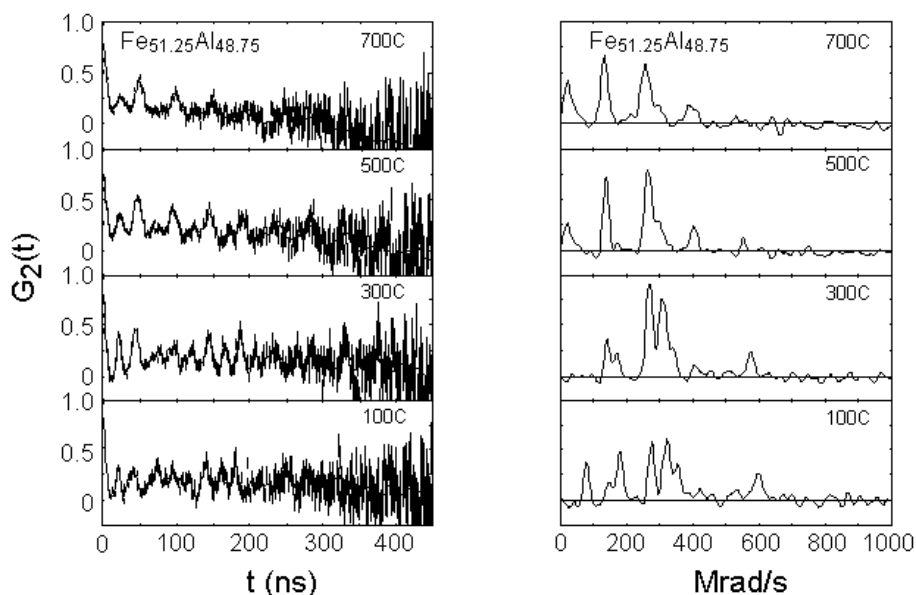
### INTRODUCTION

There is considerable current interest in properties of point defects in high-temperature structural intermetallics. Previously, we applied the method of perturbed angular correlation of gamma rays (PAC) to study point defects in NiAl both after quenching [1] and at high temperature [2]. Here, we use PAC to study defects in the B2 phase of FeAl in the range 49.5 to 54.7 at.% Fe. Structural point defects in off-stoichiometric samples of both FeAl and NiAl are known to be transition-metal (TM) antisite atoms for TM-rich compositions (e.g.,  $\text{Fe}_{\text{Al}}$ ) and TM-vacancies for TM-deficient compositions (e.g.,  $V_{\text{Fe}}$ ). The existence of these structural defects suggests that the high-temperature equilibrium combination of point defects that preserves the local composition should be the triple defect ( $2V_{\text{Fe}} + Fe_{\text{Al}}$ ). Measurements were made at elevated temperature to determine properties of point defects in FeAl.

### EXPERIMENT

Samples of  $\text{Fe}_{1+2x}\text{Al}_{1-2x}$  with  $x$  in the range  $-0.005$  to  $+0.047$  (49.5 to 54.7 at.% Fe) were prepared by arc-melting metal constituents (purity m5N) with  $^{111}\text{In}$  activity under argon in an arc-furnace. Sample masses were typically 100 mg and In concentrations were at the part-per-billion level. Samples were then annealed for one hour at 1200 °C followed by cooling to room temperature over about 10 hours. Measurements were made in a standard 4-detector PAC spectrometer and data were analyzed as described previously [3]. In Fig. 1 are shown PAC spectra for a sample with 51.25 at.% Fe measured at different temperatures. For this composition, the deviation from stoichiometry implies

a structural defect concentration of  $\text{Fe}_{\text{Al}}$  equal to 2.5 at.%. The spectra exhibit superpositions of quadrupole precession patterns for probe atoms in different local environments. The amplitude of each signal is equal to the fraction of sites in the corresponding environment. Based on its large size and valence and other arguments, the In probe should be found only on the Al-sublattice. For a probe atom without nearby defects, the point symmetry is cubic and the quadrupole frequency is zero. A low frequency signal is clearly visible in the spectra measured at 700 and 500 °C, but not at lower temperature. The high frequencies observed in Fig. 1 come from one or more point defects in the closest atomic shell. From systematics of quadrupole frequencies in a range of similar B2 compounds [4], all signals having frequencies greater than  $\sim 50$  Mrad/s can be attributed to different numbers of  $V_{\text{Fe}}$  in the closest atomic shell around the probes. If the spectra were to exhibit simple thermal activation of defects with increasing temperature, then the vacancy-free (low-frequency) signal would be most prominent at low temperature where there would be fewer defects. However, just the opposite is observed, from which we conclude that there must be a large quenched-in vacancy concentration and attractive interactions between Fe vacancies and the oversized PAC probes.

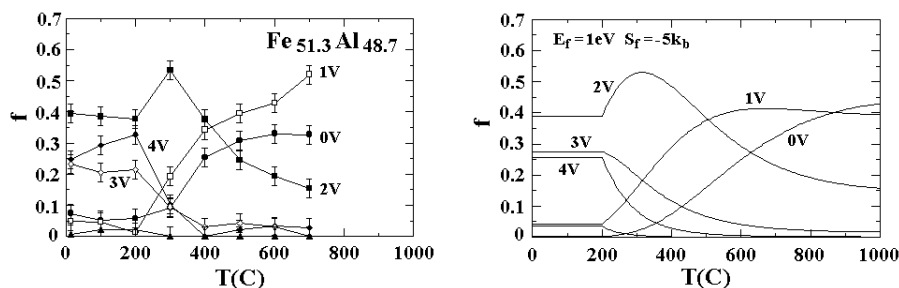


**Figure 1.** PAC spectra of FeAl (left) measured at the indicated temperatures, with corresponding frequency amplitude spectra on the right.

The 700 °C spectrum is dominated by signals with fundamental frequencies of  $\sim 0$  Mrad/s (vacancy-free), 141 Mrad/s (1V complex), and 276 Mrad/s (2V complex). (The attributions are justified below). The site fraction of the 2V signal is somewhat larger at 500 °C. At 300 °C, the 2V signal has increased greatly at the expense of the 1V and a new 180 Mrad/s signal attributed to a 3V complex is observed. Finally, at 100 °C, the 1V and 2V signals have become quite small, the 3V signal has increased and a new 70 Mrad/s signal has appeared that is attributed to a 4V complex. The trend toward trapping more vacancies at low temperature is a consequence of quenched-in but mobile vacancies and an attractive vacancy-probe interaction. In effect, vacancies “condense” on probes as temperature decreases and “evaporate” reversibly as temperature increases. Similar trends were observed for 49.5, 50.2 and 52.8 at.% Fe.

The site fractions of the complexes are shown at these and other temperatures in Fig. 2, left, together with a simulation of the trends to the right that will be described below. In order to facilitate understanding of the trends, curves in the figure are identified by attributions to vacancy complexes

listed in Table 1 below rather than by frequencies. As can be seen, there are large changes in site fractions above 200 °C, while below that temperature the motion of vacancies is too sluggish to allow vacancies to even make a few lattice-jumps and trap at the probes during the measurement times of about a day.



**Figure 2.** Left: Site fractions of PAC signals in FeAl measured at the indicated temperatures, using identifying labels from Table 1. Right: Simulation of site fractions.

Table 1 lists quadrupole interaction parameters near room temperature for the five vacancy complexes detected and, for four of them, attributions to specific structures shown in Fig. 3. With less certainty, the fifth complex is believed to involve 5 vacancies. In the table columns are listed the fundamental interaction frequency  $\omega_1$ ,  $\omega_1$  normalized by the 1V frequency, the asymmetry parameter of the electric-field gradient tensor  $\eta$ , the attribution to a type of vacancy complex, reference to a structural diagram in Fig. 3, and the normalized frequency and asymmetry parameter calculated for diagrammed complexes in the point charge approximation. Finally, it may be noted that fits of low frequency components show that  $\text{Fe}_{\text{Al}}$  antisite atoms (in the second atomic shell) produce by themselves a quadrupole frequency of only 20 Mrad/s and do not disturb the signals due to vacancies in the first shell.

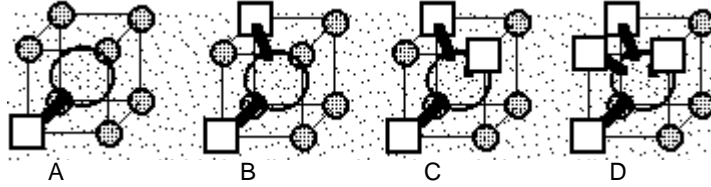
**Table 1.** Quadrupole interactions detected in FeAl attributed to vacancy complexes.

Signal	$\omega_1$ (Mrad/s)	$\frac{\omega_1}{\omega_1(1V)}$	$\eta$	Type of complex	Structure in Fig. 3	Point-charge calc.	
						$\omega_1 / \omega_1(1V)$	$\eta$
1	141(1)	(1)	0	1V	a	(1)	0
2	276(1)	1.96	0.85(1)	2V	b	1.76	1.0
3	180(1)	1.28	0	3V	c	1.00	0
4	70(1)	0.50	0	4V	d	0	0
5	336(3)	2.38	0.75(2)	5V?	-	-	-

## ANALYSIS AND RESULTS

### Identification of vacancy complexes by their quadrupole interactions

Quadrupole interaction parameters were compared with known parameters of complexes in NiAl-type B2 compounds [4]. Signals 1 and 2 fit in well with the systematics for 1V and 2V complexes [4], with the likely structure of the 2V complex shown in Fig. 3(b). There exists no data for higher-order vacancy complexes, so interaction parameters for those were compared with calculations of electric-field gradients in the point-charge approximation (neglecting lattice relaxation) for various complex structures. For the 3V complex, the best match comes from the structure in Fig. 3(c), which, like the 1V complex, has a three-fold axis of symmetry, keeping  $\eta=0$  even if the probe atom were to relax along the symmetry axis. Among 6 possible 4V structures, good agreement was found for the one in Fig. 3(d), for which the observed non-zero frequency has to be explained by a small atomic relaxation of the probe atom along the  $\langle 111 \rangle$  symmetry axis. Interestingly,  $V_{\text{Fe}}$  appear to avoid adjacent sites on their own sublattice.



**Figure 3.** Structure of vacancy complexes in FeAl. Fe atoms (small circles) and vacant sites (squares) surround the probe atom (large circles).

### Thermodynamics of defects and site fractions

Equilibrium and quenched-in defects are assumed to be triple defects ( $2V_{\text{Fe}} + \text{Fe}_{\text{Al}}$ ), with the constituting elementary defects located at random. Using the law of mass action, it can be shown that the equilibrium fractional concentration  $[V]$  of  $V_{\text{Fe}}$  is given by the cubic equation

$$[V]^3 + 4x[V]^2 = 2K = 2\exp(S_F/k_B)\exp(-E_F/k_B T) \quad (1)$$

in which  $K$  is the equilibrium constant of the formation reaction,  $x$  is the deviation from stoichiometry, and  $S_F$  and  $E_F$  are the entropy and enthalpy of formation of the triple defect. Also using the law of mass action, the site fraction for monovacancy complexes  $f_1$  can be written in terms of the site fraction for vacancy-free probes  $f_0$  as

$$f_1 / f_0 = 8[V] \exp(E_{B1} / k_B T). \quad (2)$$

Here,  $E_{B1}$  is the binding enthalpy of the first vacancy to the probe and 8 is the number of ways in which a vacancy can be placed in the first shell. Similarly, it can be shown that  $f_2 / f_1 = \frac{7}{2}[V] \exp(E_{B2} / k_B T)$  in which  $E_{B2}$  is the binding enthalpy of a second vacancy to the monovacancy complex, and so on up to  $f_8 / f_7$ . Using the set of eight fraction-ratio equations and the fact that the fractions sum to unity, one can solve for the nine site fractions for specified values of  $x$ ,  $T$ ,  $S_F$ ,  $E_F$ , and the eight binding enthalpies  $E_{Bn}$ .

### Simulation of site fractions over the range 20–700 °C

Site fraction curves in Fig. 2 (right) were computed using the method just described, but with a constant “background” vacancy concentration  $[V_0]$  added to the thermally-activated concentration to account for the large quenched-in vacancy concentration. We expect  $[V_0]$  to correspond to the equilibrium vacancy concentration at about 600 °C, below which vacancies are quenched-in.

### Low-temperatures (20–200 °C)

Below 200 °C, there is no vacancy motion. Site fractions depend sensitively on  $V_0$  and the set of values  $E_{Bn}$ . The binding enthalpies are all highly constrained.  $E_{B1}$  was determined with good precision by finding the value which gave a consistent variation of  $V_0$  with  $x$  for four samples in the range  $x = -0.005$  to  $x = 0.028$ . Best values obtained of the binding enthalpies of the first four vacancies for the four samples were 0.23, 0.23, 0.15 and 0.18 eV, respectively, with uncertainties of about  $\pm 0.02$  eV. The value  $E_{B1} = 0.23$  eV can be compared with 0.18–0.24 eV obtained for NiAl [2].

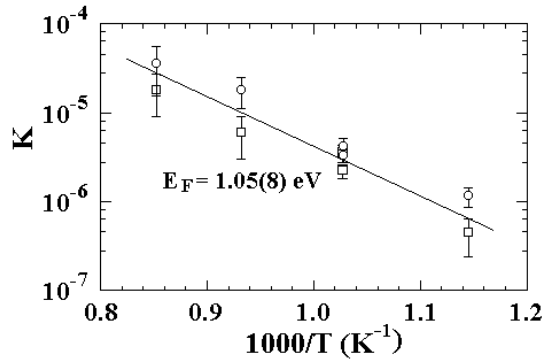
### Intermediate-temperatures (200–700 °C)

Vacancies start to move over atomic distances at about 200 °C, but below 600 °C the thermal formation of defects is very small compared to the quenched-in concentration  $[V_0]$ . Thus, changes observed in Fig 2 are from establishment of local equilibria between trapped vacancies and a constant concentration of untrapped vacancies. In the range 500–700 °C, some thermal activation takes place and the total vacancy concentration was approximated by the sum of  $[V_0]$  and the thermally activated

concentration given by Eq. 1. For this, the value  $E_F = 1.1(1)$  eV determined from high-temperature fits was used (see below).  $S_F$  could not be determined with any accuracy from the high-temperature fits described below. However, adjustments in the simulations yield the rough estimate  $S_F \approx -5 k_B$ . Interestingly, this value is close to  $S_F = -3.2(4) k_B$  obtained from high-temperature data for NiAl [2].

#### High-temperature equilibrium

Measurements were made on two samples with 52.7 and 54.7 at.% Fe at temperatures between 600 and 900 °C. Beyond 900 °C, nuclear relaxation sets in due to localized diffusion near the probes [5] and measured site fractions become uncertain. Vacancy concentrations were calculated at each temperature using measured ratios  $f_f/f_0$  and the binding enthalpy  $E_{Bf} = 0.23$  eV. Ignoring possible background contributions  $[V_0]$ , the equilibrium constant  $K$  was computed using Equation 1 and the composition parameter  $x$ . It should be noted that derived values of  $K(T)$  for the different samples overlap fairly well although the vacancy data for different  $x$  do not. In Fig. 4 is shown an Arrhenius plot of  $K(T)$ , with the best fit indicated by the straight line and yielding  $E_F = 1.05(8)$  eV. Allowing for some quenched-in defects would increase the value of  $E_F$ , so the reported value may be a little low.



**Figure 4.** Equilibrium constant for formation of the triple defect in FeAl, from measurements on samples with 52.7% Fe (circles) and 54.7% Fe (squares)

## DISCUSSION

#### Negative formation entropy

For both FeAl and NiAl [2], PAC measurements can be explained by negative values of the formation entropy of the triple defect. This would be a very surprising result. The formation entropy of a defect reflects changes in the vibrational frequencies of the lattice when the defect is created [6]:

$$S_F = k_B \ln \left\{ \prod \left( \frac{n_0}{n} \right) \right\} \quad (3)$$

in which  $\nu_0$  and  $\nu$  are vibration frequencies before and after introducing the triple defect and the product is over all vibrational modes. In many solids, introducing a defect decreases the frequencies, overall, making  $S_F$  positive and increasing the equilibrium concentration (see, for example, eq. 1). If one supposes for example that introducing a vacancy into the *bcc* structure has the effect of breaking bonds with its near-neighbors, and assumes an Einstein vibrational model, it can be shown that the formation entropy of one vacancy is  $+1.9 k_B$ . Measured values are in the range  $+1-3 k_B$  for vacancies in *fcc* metals and the range  $+6-12 k_B$  for Schottky and Frenkel defects in alkali and silver halides [7]. The negative value of  $S_F$  suggested here indicates that triple defects in NiAl or FeAl increase vibrational frequencies, as opposed to the reduction generally observed for vacancies. A possible explanation has to do with the well-known  $1/3 \langle 111 \rangle$  soft-mode instability in many *bcc* and *B2* materials (for example causing the  $\alpha$ - $\omega$  allotropic phase transformation in Zr metal). We speculate that triple defects disrupt this instability, thereby leading to an overall increase in lattice frequencies.

There are two other explanations for the apparent negative value of  $S_f$  to consider. (1) The entropy of binding between a vacancy and the probe atom has not so far been considered. This is given by eq. 3 if numerators and denominators are identified with frequencies in the situations when the vacancy is not, or respectively is, next to the probe atom. The binding entropy would have to be large and negative, which is considered very improbable. (2) Given the very high vacancy concentrations in FeAl, defect-defect interactions may limit the validity of the law of mass action used to obtain eqs. 1 and 2. It is interesting to note that the structures of the multivacancy complexes in Fig. 3 are consistent with the notion that  $V_{Fe}$  avoid each other on adjacent sites on their own sublattice or, equivalently, that they tend to cluster on (111) planes. A repulsive vacancy-vacancy interaction would have the effect of suppressing defect formation at high defect concentrations, leading to an artificially low value of  $S_f$ . Of course, this explanation could not apply as much to NiAl, where  $S_f$  is distinctly negative but in which thermal defect concentrations are more than a factor of ten lower [2].

#### *Onset of vacancy motion in FeAl at about 200 °C*

Over daylong periods, diffusion over a few lattice distances ceases below about 200 °C in either NiAl [1] or, as shown here, FeAl. Measurements made at low temperature after slowly cooling Fe-rich samples showed large fractional concentrations of quenched-in  $V_{Fe}$ , of the order of 1 at.%. These concentrations are not observed to anneal out below about 500 °C. Thus, in FeAl there is a range of several hundred degrees in which vacancies move over atomic length scales and can contribute to climb processes without annealing out, in the same way as was found for NiAl [1]. In NiAl, the onset of vacancy motion was found to be correlated with the brittle-to-ductile transition in mechanical properties [1]. Similar correlations are expected to exist for FeAl.

#### SUMMARY

PAC has been found to be a powerful method for studying point-defect phenomena in FeAl. Under the assumption that the triple defect is the dominant equilibrium defect combination in FeAl, PAC site fractions were analyzed to obtain an activation enthalpy of formation of 1.1(1) eV. A large quenched-in concentration of Fe-vacancies was observed below about 600 °C. Fe-vacancies move in day-long intervals at about 200 °C and trap at In probe atoms to form a number of multi-vacancy complexes. Attributions of PAC signals were made to complexes involving 1-4 Fe-vacancies. From simulations of equilibrium site-fractions measured over the range 200-700 °C, binding enthalpies of about 0.2 eV were determined for the first through fourth vacancies. Simulations in an intermediate temperature range suggested that the formation entropy of the triple-defect is negative.

#### ACKNOWLEDGMENT

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