



Investigations of Zr–Ni intermetallic compounds by perturbed angular correlations



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ABSTRACT

The hyperfine interactions experienced by ¹⁸¹Ta in ZrNi₅ and Zr₂Ni₇ intermetallic compounds have been investigated by the perturbed angular correlation (PAC) technique. In ZrNi₅, a strong electric quadrupole interaction (~40%) with $\omega_Q=72.0(1)$ Mrad/s, $\eta=0.25(1)$, $\delta=0$ at room temperature has been found due to the presence of Zr₂Ni₇ contaminating phase produced during sample preparation in the arc furnace. A weak quadrupole interaction of Zr₂Ni₇ (~5%) with $\omega_Q=65(1)$ Mrad/s, $\eta=0.24(6)$, $\delta=0$ has also been observed. The cubic component of ZrNi₅ also has been observed (~40% at room temperature) in this sample along with associated defect (15%). It is found that at 873 K, the cubic fraction increases to ~54% at the cost of its defect fraction. No magnetic interaction in ZrNi₅ has been observed which supports the earlier PAC results but rules out the result of strong magnetic ordering found from magnetization measurement. In Zr₂Ni₇, two regular fractions corresponding to two different crystallographic sites of Zr have been clearly identified with the parameters $\omega_Q(1)=70.9(1)$ Mrad/s, $\eta(1)=0.28(1)$, $\delta=1.3(3)\%$ and $\omega_Q(2)=64(1)$ Mrad/s, $\eta(2)=0.34(8)$, $\delta=0$ while contradictory results were reported from previous measurements.

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1. Introduction

Due to numerous technological applications, Ni based alloys are subject of recent investigations [1–3]. The MNi₅ (M=Hf/Zr) systems are found to be, particularly, interesting. This is because, in ZrNi₅, magnetization measurements by Amamou et al. [4] and electronic structure calculation by Turek et al. [5] provided no evidence for magnetic ordering at temperatures above 4.2 K. A very weak itinerant ferromagnetism was found [6] in M–Ni alloys beyond a critical Ni concentration of approximately 90 at%. Interestingly, Drulis et al. [7] observed a strong ferromagnetic ordering in ZrNi₅ with a Curie temperature of 647 K from their magnetization vs. temperature. From recent perturbed angular correlation (PAC) measurements [3], however, no magnetic interactions in MNi₅ were found. Any magnetic interaction present in a sample can easily be detected from the measurement of magnetic hyperfine field using the PAC technique [8].

The MNi₅ systems are known to have cubic symmetry (AuBe₅ type structure) with zero electric field gradient (EFG). Therefore, in absence of any magnetic ordering, a flat unperturbed angular correlation is expected from PAC measurements since, no EFG is experienced at the probe site in the crystal with cubic symmetry. From previous measurements by Silva et al. [3], electric quadrupole

interactions in MNi₅ were found to be due to the presence of contaminating phases of M₂Ni₇ which were produced during sample preparation in argon arc furnace at high temperature and subsequently cooled at room temperature. After annealing at high temperature, Silva et al. [3] concluded that the contaminating phases M₂Ni₇ disappeared and there was no magnetic interaction in MNi₅.

From previous measurements in M₂Ni₇ [3,9], contradictory results were reported for the M sites. Silva et al. [3] reported a single Hf site in Hf₂Ni₇ while Marszalek et al. [9] reported two non-equivalent M sites in both Hf₂Ni₇ and Zr₂Ni₇ with equal site percentages. Considering above facts, it seems worthwhile to re-investigate ZrNi₅ and Zr₂Ni₇ by PAC to confirm the presence or absence of any magnetic interaction in ZrNi₅ and the site occupancies in Zr₂Ni₇.

2. Experimental details

The sample ZrNi₅ has been prepared by melting stoichiometric amounts of Zr and Ni in an argon arc furnace. The metallic elements Zr and Ni were obtained from M/S Alfa Aesar. The purity of Zr was ~95% (maximum Hf concentration 4.5 wt%) and Ni purity was 99.98%. At first, the two metals were melted in the argon atmosphere of arc furnace. A shiny globule was found to be formed. A small piece of active ¹⁸¹Hf metal (~2 mg) was then added to it and the metals were remelted to produce a homogeneous solid solution.

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The natural Hf metal ($\sim 30\%$ ^{180}Hf) was pre-activated to ^{181}Hf in the CIRUS reactor at Mumbai, India through the capture of thermal neutrons for seven days (flux $\sim 10^{13}/\text{cm}^2/\text{s}$). The resulting sample was then used for PAC measurements. Due to chemical and structural similarity of Hf and Zr, it is expected that the probe ^{181}Hf resides on regular Zr sites. We are actually measuring on the ^{181}Ta impurity produced in the β^- decay of ^{181}Hf . But, in metals, there will be no effect of impurity on the PAC spectrum. For high temperature measurements, the sample was sealed in an evacuated quartz tube and was put inside a resistive furnace placed at the center of the PAC setup.

A four detector TDPAC spectrometer with BaF_2 detectors (50.8 mm dia \times 50.8 mm ht) has been used for measurements. Four coincidence combinations (two at 180° and two at 90°) have been formed with these four detectors. The perturbation function $G_2(t)$ has been obtained from the ratio of coincidence counts at 180° and 90° . The TDPAC measurements have been carried out using the 133–482 keV cascade of ^{181}Ta with its intermediate half-life of 10.5 ns [10], populated in the decay of ^{181}Hf ($T_{1/2} = 42$ d). The prompt time-resolution (FWHM) for these two γ -rays was found to be ~ 0.9 ns. The detector distances were 7 cm from the source. Details about the experimental setup and data acquisition have been described in our earlier report [11].

The influence of quadrupole interaction on the γ - γ angular correlation in polycrystalline samples is described by the perturbation function $G_2(t)$ given by [12], $G_2(t) = [S_{20}(\eta) + \sum_i^3 S_{2i}(\eta) \cos(\omega_i t) \exp(-\delta\omega_i t) \times \exp[(\omega_i \tau_R)^2/2]]$ for the spin angular momentum $I = 5/2$ of the intermediate level. The first exponential term is a measure of the imperfection in the crystal where, δ is the value of the frequency distribution width of the Lorentzian distribution. Finite time resolution of the coincidence setup (τ_R) has been considered through the second exponential. Here, the three frequencies ω_i correspond to transitions between the sublevels of the spin $I = 5/2$. These sublevels appear due to the interaction of the nuclear quadrupole moment with the local EFG (hyperfine splitting). The three interaction frequencies ω_i are related to the nuclear electric quadrupole interaction (NQI) frequency ω_Q by $\omega_Q \equiv \omega_1/6 \equiv \omega_2/12 \equiv \omega_3/18$ for the asymmetry parameter $\eta = 0$. The ω_Q and η are defined as $\omega_Q = eQV_{zz}/4I(2I-1)\hbar$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx} , V_{yy} and V_{zz} are the elements of the EFG tensor in its principal axis system. If the intermediate nuclear state experiences more than one electric field gradient, the TDPAC spectra are generally fitted to the theoretical function $A_2 G_2(t) = A_2 \sum_i f_i G_2^i(t)$, with f_i the fraction of i -th component present in the sample and $G_2^i(t)$ its corresponding perturbation function.

3. Results and discussion

The spectrum obtained for ZrNi_5 at room temperature in the as prepared sample is shown in Fig. 1. It is found that instead of flat perturbation due to its cubic structure, it produces a strong perturbation. Analyzing the spectrum, perturbation due to electric quadrupole interaction is only obtained. In fact, the spectrum can be best fitted by considering three electric quadrupole interactions. The sample is found to have texture effects and it does not exhibit a perfectly polycrystalline nature which means the electric field gradients generated at the probe site are not randomly oriented and the values of S -coefficients will not be same as those for a powder sample. This is clearly evident from the peak intensities in the Fourier transforms. The spectra at different temperatures are therefore fitted with free S_{kn} coefficients for the main component. The results are shown in Table 1. The point to note is that no magnetic interaction is required to fit the data, but, requires three electric quadrupole frequencies. The main frequency component ($\sim 40\%$) gives $\omega_Q = 72.0(1)$ Mrad/s, $\eta = 0.25$

(1) and $\delta = 0$. The results for other two minor components are given in the table. Interestingly, the PAC spectrum shows a large base line shift indicating a significant fraction of the probe does not experience any perturbing interaction. This fraction ($\sim 40\%$) can therefore be considered as the cubic ZrNi_5 . The percentage site fractions of different components have been found from the relative amplitudes of the fitted spectra. The two static frequency components (1 and 2) observed here have been assigned to Zr_2Ni_7 . The component 3 (15%) has been assigned to the defect ZrNi_5 . The assignment of components 1 and 2 has been confirmed from a separate TDPAC measurement in Zr_2Ni_7 at room temperature. The component 3 is assigned from temperature dependent measurements in ZrNi_5 described in the following section. It was found from previous report [3] that during preparation of ZrNi_5 in the arc furnace, Zr_2Ni_7 is produced along with unreacted Ni. This was confirmed from XRD measurements [3]. In the present as prepared sample also, Ni deficient Zr_2Ni_7 is found to be formed. While Zr_2Ni_7 is observed from PAC measurements, any magnetic interaction due to Ni precipitation is not found, probably, due to its very small interaction compared to strong electric quadrupole interactions. In a well annealed sample, the Zr_2Ni_7 recombine with unreacted Ni and produced a complete ZrNi_5 phase where no quadrupole interaction due to Zr_2Ni_7 was observed [3].

To identify and confirm the components observed in ZrNi_5 which has a cubic symmetry with zero EFG, we have prepared a Zr_2Ni_7 intermetallic compound in the similar manner as in ZrNi_5 and performed the TDPAC measurement at room temperature. It is known that Zr_2Ni_7 crystallizes in a monoclinic crystal structure with $C2/m$ space group symmetry. The spectrum in Zr_2Ni_7 at room temperature is shown in Fig. 2. Here also, the texture effect in the sample is clearly evident from the Fourier peaks. The spectrum is therefore fitted with free S_{kn} coefficients for the principle component 1. The results obtained in Zr_2Ni_7 at 298 K are shown in Table 1. In this sample, three quadrupole frequency components have been observed and interestingly, the values of quadrupole frequencies for the two components agree with those found in ZrNi_5 sample. This proves that the two quadrupole frequency components (1 and 2) observed in ZrNi_5 were due to the contaminating phase of Zr_2Ni_7 and these were produced along with unreacted Ni during sample preparation in the arc furnace at high temperature. The site fractions for the two fractions of Zr_2Ni_7 are found to be 84% and 9% for the components 1 and 2, respectively (Table 1). The third weak component in this sample (7%) is the defect ZrNi_5 . After annealing the sample, these results are found to be practically unchanged. From temperature dependent PAC measurements [13], it has been found that components 1 and 2 are two regular fractions of Zr_2Ni_7 .

In ZrNi_5 sample, measurements have been performed at higher temperatures also, particularly to identify the third component (15% at RT) observed. The results obtained at different temperatures are shown in Table 2. The corresponding spectra are shown in Fig. 1. It is found that as temperature increases, the two regular fractions corresponding to Zr_2Ni_7 do not change much and their total fractions remain almost same as found at room temperature. But, with increase in temperature, the relative shift of the base line increases indicating an increase of the ZrNi_5 cubic fraction. On the other hand, the fraction for the third frequency component decreases to 5% compared to the fraction observed at RT (15%). So, the third component can be assigned to the defect fraction of cubic ZrNi_5 . At higher temperatures, the regular cubic fraction of ZrNi_5 increases at the cost of its defect fraction (Fig. 3).

The PAC measurement in ZrNi_5 has been also performed at liquid nitrogen temperature to reveal any magnetic interaction at lower temperature. For this, the source is immersed in a small liquid nitrogen dewar which was placed at the center of the PAC table. The result (Table 2) shows that at 77 K, only one component

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