Electric Quadrupole Interaction at ^{181}Ta in Isostructural Orthorhombic Cu_8Hf_3 and Cu_8Zr_3 Compounds*

P. Wodniecki, B. Wodniecka, A. Kulińska, and A. Z. Hrynkiewicz
H. Niewodniczański Institute of Nuclear Physics, 31-342 Cracow, Radzikowskiego 152, Poland

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The quadrupole interaction of ^{181}Ta probes in isostructural Cu_8Hf_3 and Cu_8Zr_3 intermetallic compounds was studied in the temperature range 24 K – 1100 K with the time-differential perturbed angular correlation technique. Two nonaxial electric field gradients corresponding to two nonequivalent hafnium or zirconium sites in the investigated structure were found. A linear decrease in the quadrupole interaction frequency with increase of temperature for the 8(d) sites was evidenced, while the $\nu_Q(T)$ dependence for the 4(c) sites is weaker and has a $T^{3/2}$ character.

Key words: Hyperfine Interactions; Perturbed Angular Correlations; EFG; Intermetallic Compounds; Cu-Hf and Cu-Zr Systems.

1. Introduction

In view of recent progress in the theoretical description of electric field gradients (EFG's) in metals it is important to enlarge the available base of experimental data. The perturbed angular correlation technique (PAC), due to its sensitivity to the nearest charge distribution around the probe atoms, is highly suitable for such experiments. The change of the EFG with temperature follows for most metal systems the $T^{3/2}$ law [1]. Such temperature dependence was understood as originating mainly from the lattice vibrations and thermal expansion [2]. There are, however, cases where a $T^{3/2}$ dependence is not observed [3–6].

The first observation of a peritectic phase with about 70 at.% Cu in the Cu-Zr system was made by Lundin et al. [7]. Later Bsenko [8, 9] found that this most copper rich Cu_8Zr_3 peritectic phase is orthorhombic (*Pnma* space group) and is homogeneous near to 78 at.% Cu. Two nonequivalent sets of Zr atoms and six of Cu occur in the structure. X-ray powder diffraction data [9] show that Cu_8Zr_3 is isostructural with Cu_8Hf_3.

2. Experimental Details and Data Analysis

The Cu_8Hf_3 and Hf doped $Cu_8Zr_{2.94}Hf_{0.06}$ samples were prepared by argon arc melting followed by an annealing in sealed and evacuated quartz tubes at 900 °C for 150 hours. The powder X-ray analysis verified a single-phase product of the reported structure for both specimens. The samples were neutron irradiated in order to produce the $^{181}Hf(\beta^-)^{181}Ta$ activity and annealed to remove the irradiation defects. The PAC measurements with ^{181}Ta were performed using a standard four BaF_2 detector setup with time resolution of 0.8 ns for the energies 134 keV and 482 keV.

The perturbation factor

$$G_2(t) = \sum_{i=1}^{n} f_i \sum_{n=0}^{3} [s_{2n}(\eta_i) \cos(g_n(\eta_i)\, \nu_{Qi}\, t) \cdot \exp(-g_n(\eta_i)\, \delta_i\, t)], \qquad (1)$$

least squares fitted to the experimental PAC spectra, yielded the values of quadrupole frequencies ν_Q and asymmetry parameters η. Both investigated samples showed evidence of non-random orientation of the crystallites, and the PAC data had to be fitted with free s_{2n} parameters. The PAC method is described in details in [10, 11].

3. Results

The PAC spectra were recorded in the temperature range 24 K – 1100 K. The room temperature data are presented in Figure 1 with the corresponding Fourier transforms.

The least squares fits of the perturbation factor to the experimental spectra yielded for each sample two fractions f_i ($i = 1, 2$) of probe atoms exposed to different EFG's corresponding to quadrupole frequencies

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Reprint requests to Dr. P. Wodniecki, Fax: 0 48-12-6 37 02 22.

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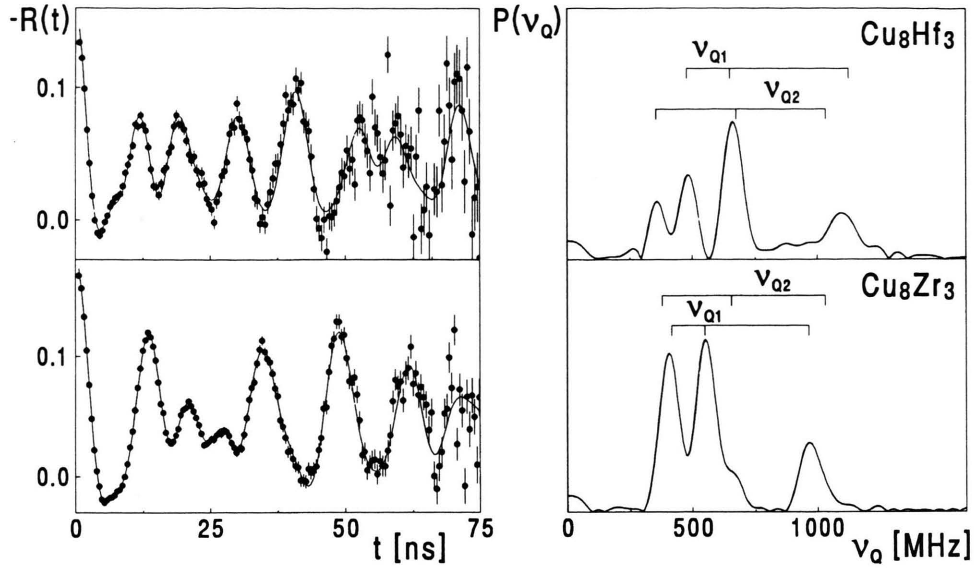

Fig. 1. Room temperature PAC spectra (with corresponding Fourier transforms) for ^{181}Ta in Cu_8Hf_3 and Cu_8Zr_3 compounds.

Compound	ν_Q(300 K) [MHz]	η(300 K)	V_{zz}^{exp}(300 K) [10^{17} Vcm^{-1}]	ν_Q(0) [MHz]	a[10^{-4} K^{-1}] b[10^{-5} K$^{-3/2}$]	attributed lattice site
Cu_8Zr_3	295(3)	0.68(1)	±5.17(5)	329(3)	$a = +3.81(7)$	8(d) 1
	336(3)	0.33(1)	±5.89(5)	348(3)	$b = +0.69(8)$	4(c) .m.
Cu_8Hf_3	349(3)	0.64(1)	±6.12(5)	385(3)	$a = +3.50(5)$	8(d) 1
	336(4)	0.22(3)	±5.89(7)	342(5)	$b = +0.46(4)$	4(c) .m.

Table 1. The fitted quadrupole interaction parameters of ^{181}Ta in Cu_8Hf_3 and Cu_8Zr_3.

ν_{Qi} and asymmetry parameters η_i. The $f_1 : f_2$ ratio 2:1 as well as the fitted non-zero η_i values are consistent with the predicted two non-equivalent 8(d) and 4(c) probe sites of non-axial symmetry.

Using the quadrupole moment value of the 482 keV state of ^{181}Ta ($Q = 2.36$ b [12]) the experimental values of the EFG at the probe nuclei

$$V_{zz}^{\mathrm{exp}} = h\,\nu_Q / e\,Q \tag{2}$$

were computed from the measured quadrupole interaction frequencies ν_Q and collected in Table 1.

For most metallic systems ν_Q decreases with the three-halves power of the temperature:

$$\nu_Q(T) = \nu_Q(0)\,[1 - b\,T^{3/2}], \tag{3}$$

but in some cases a linear temperature dependence was observed:

$$\nu_Q(T) = \nu_Q(0)\,[1 - a\,T]. \tag{4}$$

These formulae were used to parametrize the EFG temperature dependence in the investigated compounds. The fitted quadrupole interaction parameters are collected in Table 1. The $\nu_Q(T)$ and $\eta(T)$ curves are shown in Figure 2. The observed character of $\nu_Q(T)$ attributed to the 8(d) and 4(c) probe sites is different. For both compounds a linear decrease of the EFG at the 8(d) site, with a large slope, is evidenced. The EFG at the 4(c) site exhibits a weaker temperature variation, and better fits are obtained assuming $T^{3/2}$ character of their temperature dependence.

4. Discussion

The results of our PAC experiment are consistent with the reported crystallographic structure of Cu_8Zr_3 and Cu_8Hf_3. The substitution of Zr on Zr sites by ^{181}Ta probe atoms in the Cu_8Zr_3 sample is confirmed. The identical quadrupole frequencies corresponding to the 4(c) hafnium and zirconium sites, and the only slightly different frequencies attributed to the 8(d) crystallographic places reflect the chemical similarity

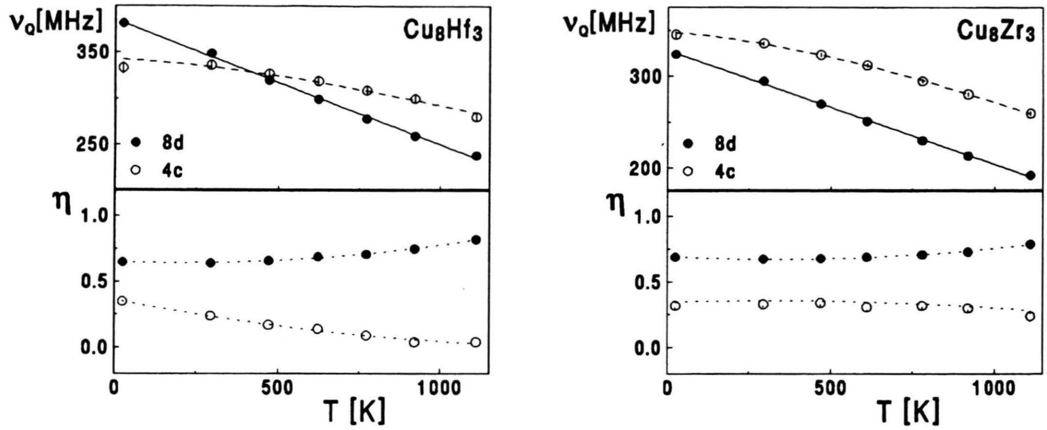

Fig. 2. The temperature dependence of quadrupole interaction parameters for ^{181}Ta in Cu_8Hf_3 and Cu_8Zr_3 samples.

of Hf and Zr and the very close lattice constants of Cu_8Zr_3 and Cu_8Hf_3.

As can be seen in Figure 2 the decrease in the quadrupole interaction frequency with increasing temperature is rather rapid for both compounds. The fitted slopes a and b of the $\nu_Q(T)$ curves are, respectively, fairly similar, which reflects the similar neighbourhood of the probe atoms in the investigated samples. The different character of the temperature dependence for 4(c) and 8(d) sites indicates the role of local lattice vibrations due to the different binding strength in unequivalent crystallographic positions of the compound. This effect was noticed also in some Pd and Pt binary compounds [13, 14] and $TiNi_3$-type intermetallic phases [15].

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