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The nuclear quadrupole interaction of ^{181}Ta in the intermetallic compound Hf_2Rh

N Ivanović, S Koički, B Cekić, M Manasijević, V Koteski and D Marjanović

Institute of Nuclear Sciences VINČA, Laboratory for Nuclear and Plasma Physics, PO Box 522, Belgrade, Yugoslavia

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Abstract. The time differential perturbed angular correlation technique has been used to measure the electric field gradient at ^{181}Ta impurities in the intermetallic compound Hf_2Rh . The results of the measurements show the presence of two independent quadrupole interactions. At room temperature the interaction frequencies are $\omega_{Q1} = 58 \text{ Mrad s}^{-1}$ and $\omega_{Q2} = 239 \text{ Mrad s}^{-1}$. The electric field gradient V_{zz} , the corresponding asymmetry parameter η and the distribution parameter δ exhibit a pronounced temperature dependence from 78 to 1223 K.

1. Introduction

Most of the nuclear quadrupole interaction (NQI) measurements in the Hf intermetallic compounds published so far [1–4] have revealed an unusual behaviour and a prevalence of the electronic contribution to the total electric field gradient (EFG). The general impression is that the origin and the magnitude of the EFG in the investigated intermetallic compounds have no simple explanation and that no elementary ‘temperature law’ of the temperature dependence of the NQI parameters can be established. This prompted us to study the NQI of ^{181}Ta in the ordered intermetallic compound Hf_2Rh , in a series of investigations of the isostructural compounds of Ti_2Ni structure type. The NQI at the Hf site was measured by observing the time differential perturbed angular correlation (TDPAC) of the gamma–gamma cascade (133 keV–482 keV) in ^{181}Ta .

2. Experiment

2.1. Source preparation and experimental setup

The Hf_2Rh samples were prepared by melting stoichiometric quantities of 99.97% pure hafnium metal (except for 2% of zirconium) and 99.98% pure rhodium metal in a radio-frequency inductive furnace. X-ray powder diffraction investigations of the samples confirmed the expected Ti_2Ni structure type of the intermetallic compound Hf_2Rh .

For the purposes of TDPAC measurements of the NQI in this compound, the samples were irradiated in a flux of thermal neutrons producing the radioactivity of the well known TDPAC-probe $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$. The irradiated samples were then annealed at 900°C for ten days, which is expected both to improve the structure and to heal defects induced by (n, γ) reaction. Small samples of only a few milligrams in weight were used as sources in TDPAC measurements that ensured negligible self-absorption of γ -rays.

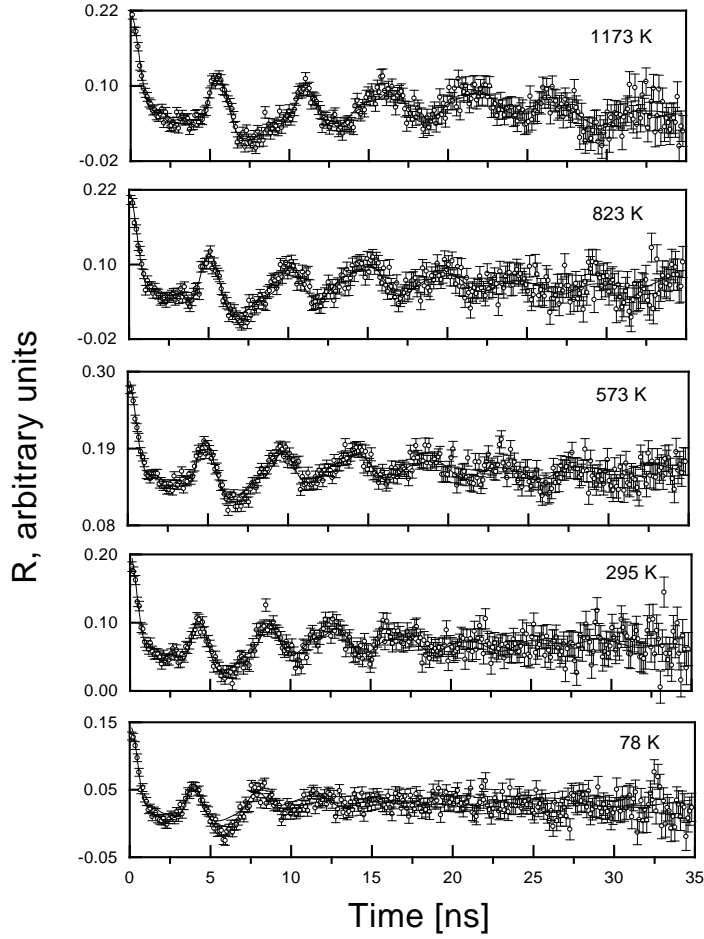


Figure 1. TDPAC spectra of ^{181}Ta in the intermetallic compound Hf_2Rh at different temperatures: —, theoretical fit.

TDPAC measurements were performed by the coincidence setup consisting of two BaF_2 -detectors, described earlier [3,4]. A good time-resolution of the coincidence system of $\tau_R = 0.5$ ns (FWHM) at the ^{181}Ta γ -energies ensured a good resolution of the NQI frequencies, characteristic for this compound.

2.2. Measurements and results

The experimental perturbation function $R(t)$ was deduced from the TDPAC-spectra measured at two different angles, $W(90^\circ, t)$ and $W(180^\circ, t)$, according to the expression [5]:

$$R(t) = 2 \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + 2W(90^\circ, t)}.$$

It was fitted to a function $A_{22}G_{22}(t)$, where A_{22} is the unperturbed angular correlation coefficient and $G_{22}(t)$ is the perturbation factor for a randomly oriented static NQI. For the

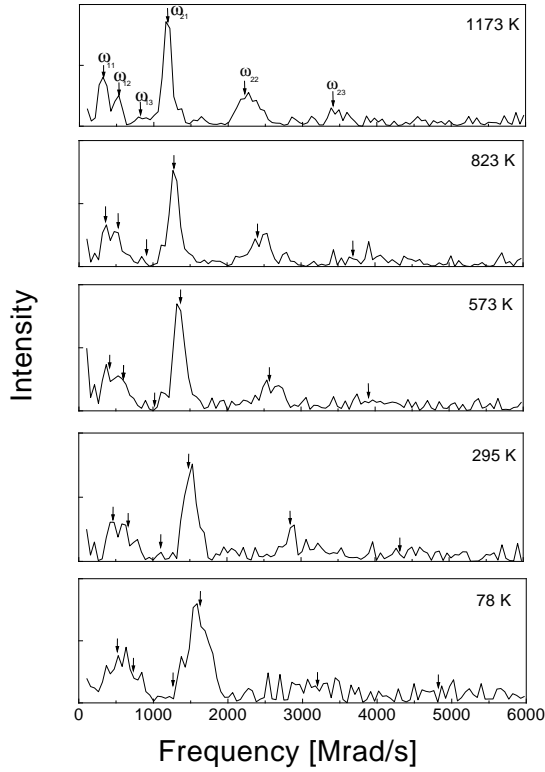


Figure 2. Fourier transformed TDPAC spectra of the intermetallic compound Hf_2Rh (in arbitrary units) at different temperatures.

nuclear spin of $I = 5/2$, the perturbation factor $G_{22}(t)$ has the form [5]

$$G_{22}(t) = a_{20} + \sum_{n=1}^3 a_{2n} \exp\left(-\frac{(\omega_n \tau_R)^2}{2}\right) \exp(-\delta \omega_n t) \cos(\omega_n t).$$

The transition energies $\hbar \omega_n$ between nuclear sublevels depend on the NQI frequency ω_Q [5],

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$$

and the EFG asymmetry parameter η . The coefficients a_{20} and a_{2n} are functions of η only. A line broadening of the oscillation amplitudes a_{2n} is introduced through the finite time resolution of the coincidence system τ_R and the distribution parameter δ of the EFG.

Measurements were performed at ten different temperatures in the range from 78 to 1223 K, and five characteristic $R(t)$ spectra are presented in figure 1. The corresponding Fourier transformed spectra are shown in figure 2. Two well resolved NQIs are observed, presumably connected with two different crystallographic sites of Hf(Ta) ions in the lattice. The positions of the transition frequencies ω_1 , ω_2 and ω_3 are also indicated in the diagram. The lack of certain ω_2 and ω_3 components is due to a relatively large distribution factor δ of the EFG.

The time-spectra from figure 1 were fitted to the expression,

$$R(t) = A_{22} \sum_{i=1}^2 f_i G_{22}^i(t)$$

Table 1. NQI parameters for ^{181}Ta impurities in Hf_2Rh at the 16c and 48f positions. $Q = 2.36(5) \times 10^{-24} \text{ cm}^2$ [14] is the value of the nuclear quadrupole moment used for V_{zz} calculations.

T [k]	ω_Q [Mrad s $^{-1}$]	η	δ	f_i (16c)		$V_{zz} \times 10^{-17}$ [V cm $^{-2}$]
				f_1 (16c)	f_2 (48f)	
16c						
78	65(3)	0.59(4)	0.07(2)	24		6.7(3)
295	58(2)	0.59(5)	0.13(3)	25		6.0(2)
52	49(2)	0.62(6)	0.16(2)	27		5.1(2)
573	51(1)	0.55(4)	0.13(3)	16		5.3(1)
723	46(1)	0.64(8)	0.20(5)	17		4.8(1)
823	46(1)	0.59(3)	0.08(3)	23		4.8(1)
873	46(1)	0.57(3)	0.09(3)	16		4.8(1)
1073	42(1)	0.61(4)	0.08(4)	22		4.4(1)
1173	44(1)	0.46(3)	0.07(2)	25		4.6(1)
1223	44(1)	0.53(4)	0.05(3)	23		4.6(1)
48f						
78	267(3)	0.13(4)	0.078(8)	75(3)		27.7(1)
295	239(2)	0.19(1)	0.053(5)	59(2)		24.8(2)
523	217(2)	0.22(6)	0.054(5)	68(2)		22.5(2)
573	215(1)	0.20(4)	0.053(4)	42(1)		22.3(1)
723	207(1)	0.20(1)	0.055(4)	38(1)		21.5(1)
823	203(1)	0.21(1)	0.053(4)	65(2)		21.0(1)
873	199(1)	0.22(1)	0.047(4)	43(1)		20.6(1)
1073	195(1)	0.16(2)	0.045(4)	64(2)		20.2(1)
1173	187(1)	0.20(1)	0.046(3)	65(1)		19.4(1)
1223	186(1)	0.18(2)	0.040(4)	68(2)		19.3(1)

allowing for two different crystallographic sites. The fitted curves are presented as full lines in figure 1. The set of obtained parameters characterizing the NQI at the two sites is presented in table 1. The relative fractions f_1 and f_2 of the two interactions, derived from the fit, match very well the expected ratio of Hf ions at the two crystallographic positions in this compound (i.e. three atoms at the 48f versus one atom at the 16c position). The temperature dependencies of ω_Q -, η - and δ -parameters for the two NQIs are plotted in figures 3–5.

3. Discussion

As follows from the presented measurements, two distinct NQIs are observed in the Hf_2Rh compound (figure 2 and table 1). They are associated with the 48f and the 16c crystallographic sites of the Hf ions in this lattice. The main features of the observed EFGs are (i) large difference (of about fourfold) in their strength at the two sites in the same lattice and (ii) high value of the EFG at the 48f site, which considerably surpasses EFGs observed to act at this probe ion in most other metallic media. Both of these observations are strikingly similar to those found in the isostructural Hf_2Fe compound [3], the difference being that in the Hf_2Rh case the EFGs at both sites are somewhat stronger.

As pointed out in [3], there is convincing experimental evidence that in the Hf_2Fe compound 3d electrons of Fe hybridize with 5d and 6s electrons of Hf. This circumstance permits a qualitative explanation of the exceptionally strong EFG found at the 48f sites. Namely, it has been shown by *ab initio* band calculations [6] that in metallic systems formed

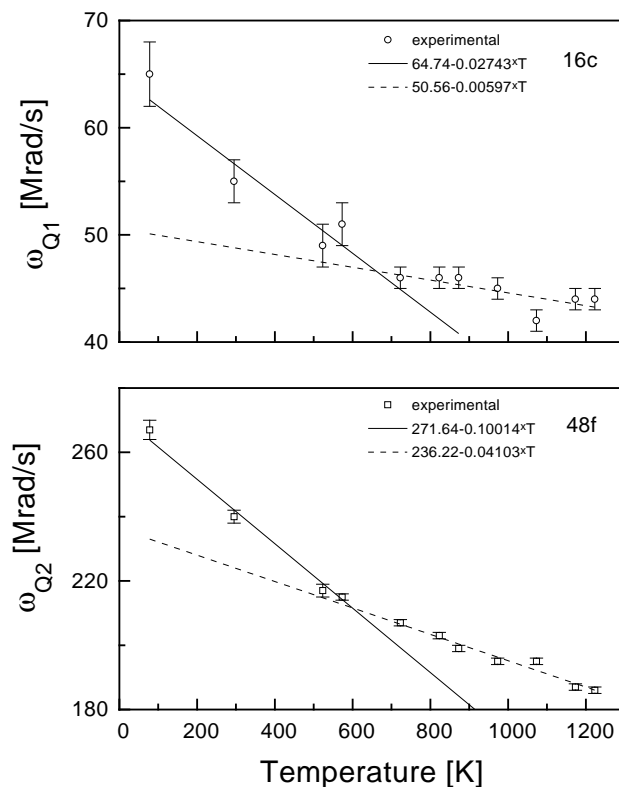


Figure 3. Nuclear quadrupole frequency ω_Q derived from the TDPAC spectra for the ^{181}Ta impurity in the intermetallic compound Hf_2Rh as a function of the temperature for the two different ^{181}Ta positions.

of ions from the beginning and the end of the d series, as is the case in this compound, d–d hybridization induces large EFGs at nuclei of ions from the beginning of the series. This effect is associated with the unoccupied antibonding states (d-hole states) of the hybridized d–d system, as the source of the major component of EFG. The same mechanism may be expected to account for the exceptionally strong EFG in the isostructural Hf_2Rh compound as observed in this study. This compound is also formed of elements from the beginning and the end of the d series, the difference being that Rh ions belong to 4d, whereas Fe ions to the 3d series. This striking similarity of observed EFGs in the two compounds may be interpreted as additional proof in favour of the proposed interpretation. A similar behaviour of EFGs may than be expected for the whole ‘sub-class’ of intermetallic compounds consisting of elements from the beginning and the end of any of d series, provided that they form hybrid bonds. Our x-ray powder diffraction [7, 8] and scanning tunnelling microscopy (STM) [9] investigations of the $\text{Hf}(2)\text{-X}$ ($X = \text{Fe}, \text{Rh}, \text{Co}$) class of intermetallic compounds show that bonds at the 48f site form two groups with strikingly different lengths (see figure 6). At present it is not certain which group of ions participates in the indicated type of bonding.

Concerning the much lower EFG value found at the 16c site, both in Hf_2Fe and Hf_2Rh , it should be pointed out that all six bonds of the probe ion to the neighbouring Fe(Rh) and Hf ions are very short, and arranged in a highly symmetrical manner [3, 7, 8], as is usual in a ‘metallic’ environment [10].

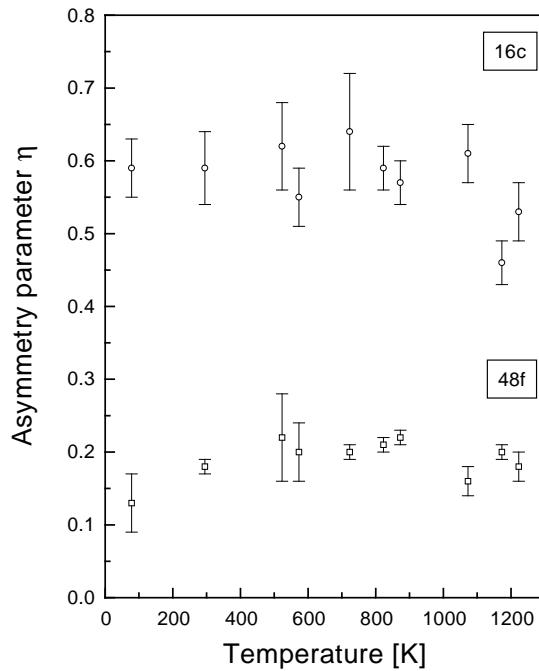


Figure 4. Asymmetry parameter η plotted as a function of the temperature for the ^{181}Ta impurity in the intermetallic compound Hf_2Rh for the two different ^{181}Ta positions.

The observed temperature dependence of the EFG at the 48f site in Hf_2Rh (figure 3) could neither be satisfactorily fitted by assuming a single linear nor by a $T^{3/2}$ -dependence. The best fit was achieved by assuming two linear sections of different slope intercepting between 600 and 650 K, which is in the temperature range of the suspected phase transition of this compound, as registered in the C_p -measurements [11]. The temperature dependence of the EFG at the 16c site (figure 3) exhibits the same behaviour, i.e. two linear sections intercepting at about the same temperature as above. These observations suggest that in this temperature range some changes in the electronic structure of the compound take place. It is interesting to note that a similar discontinuity of the EFG temperature dependence was also observed in the Hf_2Fe compound [3], where it exhibited a more pronounced manifestation (change of sign).

The temperature dependence of the asymmetry parameter η of the EFG at the two sites in Hf_2Rh is displayed in figure 4. At the 16c site it fluctuates around $\eta \sim 0.6$ and at the 48f site around $\eta \sim 0.2$. Unfortunately, the quality of the data does not allow a more specific determination of the form of the temperature dependence of η , as was the case in the Hf_2Fe compound.

Figure 5 displays the temperature dependence of the distribution parameter, δ , of the EFG at the two sites in Hf_2Rh . It is observed that this parameter has a relatively high value ($\delta \geq 0.05$) at both sites (higher at 16c) and at all temperatures. All our attempts to reduce δ , by varying the annealing procedure, have failed. It is possible that annealing procedure in this complex lattice did not sufficiently repair the specific damages induced by (n, γ) reaction. One can also not exclude that the increased value of δ in this compound presents an intrinsic property of its electronic structure. It should be noted that in the isostructural Hf_2Fe compound the δ parameter at the 48f site is at a much lower (~ 0.01) level in the whole temperature range, but not so substantially different at the 16c site [3, 8]. Although the determination of δ at the

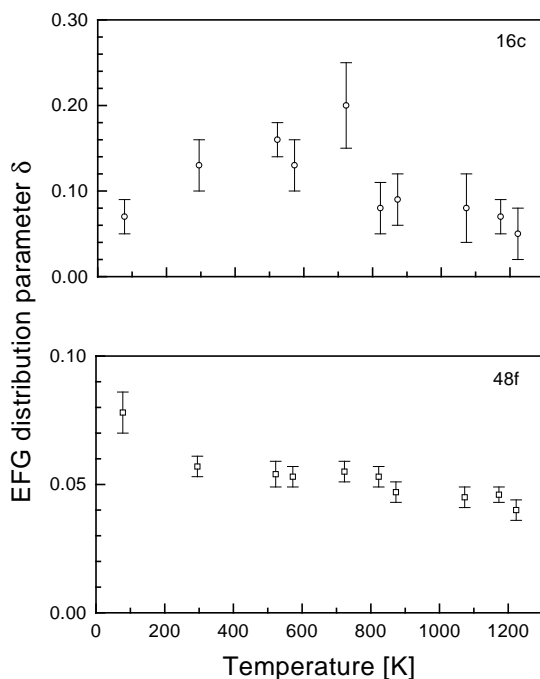


Figure 5. EFG distribution parameter δ plotted as a function of the temperature for the ^{181}Ta impurity in the intermetallic compound Hf_2Rh for the two different ^{181}Ta positions.

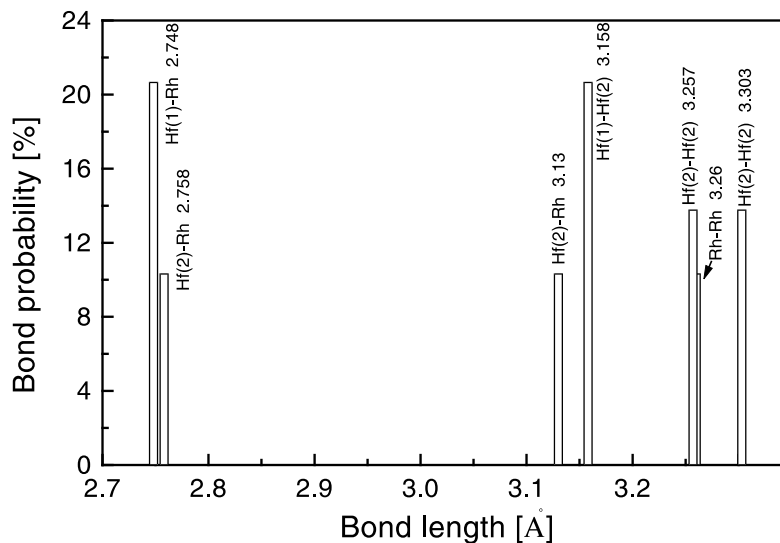


Figure 6. Bond length probability at the first coordinations of the intermetallic compound Hf_2Rh , obtained by the full profile Rietveld method refinement of the x-ray diffraction data.

16c site is fraught with considerable experimental difficulties, there is an indication that the EFG at this site exhibits the largest dispersion in the temperature range of the phase transition of this compound (see figure 5). At higher temperatures it approaches the 48f δ level.

A large fraction of ions that do not contribute the interactions $f_0 = 100 - (f_1 + f_2)$, of about 40%, appears in the phase transition temperature range (573–723 K), but also at 873 K. However, this parameter is quite sensitive to experimental conditions when the two-detector experimental set-up is used, so the results should be considered with care.

4. Conclusion

In this paper we presented TDPAC-data on the determination of EFGs acting at the nuclei of ^{181}Ta -probe ions in the lattice of the Hf_2Rh intermetallic compound. Similar data on EFGs in complex metallic systems of transition elements are generally very scarce. This is certainly due to the experimental difficulties associated with the resolution of complex time spectra, but also with the fact that traditional approaches in theoretical treatment of EFGs as a rule fail when applied to such systems. Quite recently, however, much progress has been made in modelling and calculating the electronic band structure of complex metallic systems, which has led to the development of simplified and practical methods of calculation of EFGs [6, 12]. As shown, the origin of EFGs in these systems is generally very complex, involving substantial contributions of deeper electronic shells (Hf f states for instance), as well of bonding with neighbouring ions. It seems at present that modern band calculations have become an important tool in a proper understanding of the origin and the properties of the EFGs in complex metallic systems involving transition elements.

In the case of the Hf_2Rh and Hf_2Fe compound the lattice is very complex, containing 96 atoms per unit cell [3, 7, 8]. It is well known that the difficulties of band calculations strongly increase with this number. Nevertheless, the latest developments open the possibility to treat even such systems [13], and band structure calculations of EFGs in the Hf_2Fe compound are in progress in our institute.

Experimental data such as those presented in this paper, and that of [3], offer a diversity of tests for band structure calculations of EFGs, such as *strength*, *symmetry* and *sharpness* of EFGs, as well as their dependence on temperature and position in the lattice. In addition, TDPAC together with x-ray diffraction and STM methods, when applied to the series of isostructural compounds in a wide temperature range, offer a possibility to investigate the nature of bonding, and even a single bond contribution to EFGs. This could be of importance for understanding the formation, stability and properties of intermetallic compounds in general.

Acknowledgment

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