PAC Studies of Ag-Hf Intermetallic Compounds*

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Z. Naturforsch. **51 a,** 437–441 (1996); received November 20, 1995

The hyperfine quadrupole interaction of ^{181}Ta and ^{111}Cd probes in HfAg and Hf_2Ag compounds was studied at 24 to 1100 K with the time -differential perturbed angular correlation (TDPAC) technique. The EFGs measured in HfAg on ^{181}Ta and ^{111}Cd are $1.388(5) \times 10^{18}$ Vcm^{-2} and $0.340(5) \times 10^{18}$ Vcm^{-2}, respectively. For both probe atoms a linear decrease of the EFG with temperature was observed with slopes $1.11(2) \times 10^{-4}$ K^{-1} and $1.73(5) \times 10^{-4}$ K^{-1} for ^{181}Ta and ^{111}Cd, respectively. In Hf_2Ag, $0.469(2) \times 10^{18}$ Vcm^{-2} was determined on ^{181}Ta nuclei and $0.428(5) \times 10^{18}$ Vcm^{-2} on ^{111}Cd. Also a linear EFG temperature dependence with the large slope of $2.39(6) \times 10^{-4}$ K^{-1} was observed for ^{111}Cd probes in Hf_2Ag, while the EFG measured on ^{181}Ta nuclei in this compound exhibits a very weak temperature variation which can be fitted neither with a linear T nor a $T^{3/2}$ dependence. In all cases the electronic contributions to the EFG are very small indicating that these transition element systems do not obey the universal correlation between the electronic and the ionic EFG observed in numerous other systems not belonging to the transition metal series.

Key words: Hyperfine interactions, perturbed angular correlations, electric field gradient, intermetallic compounds, Ag-Hf system.

1. Introduction

The EFG at a nuclear probe depends on the nearest charge distribution. Its determination is an excellent tool to study the electron density that depends on chemical composition of materials. A considerable number of cases has been reported for systems with transition metals where either the sign or the magnitude of the electronic EFG are incompatible with the correlation between the electronic and ionic field gradient observed in a large number of pure metals and impurity-host combinations. This suggests that in transition element systems the electronic EFG may be dominated by contributions which do not arise in simple s-p metals. The temperature dependence of the EFG provides a way to study the dynamics of the material structure and some models have been developed which allow to understand the behaviour of the EFG with temperature. The purpose of this work was to enlarge the experimental data basis on EFGs in intermetallic compounds with transition metals.

No equilibrium phase diagram is available for the silver-hafnium system. This system is supposed to be analogous to Ag–Zr and exhibits only two intermetallic compounds of tetragonal structure: the equiatomic HfAg phase ($B11$, P4/nmm) and the Hf_2Ag phase ($C11_b$, I4/mmm) [1]. The unit cells of Hf_2Ag (Hf in 4(e) 4mm and Ag in 2(a) 4/mmm positions) and of HfAg (Ag and Hf ions in 2(c) 4mm positions) are shown in Figure 1.

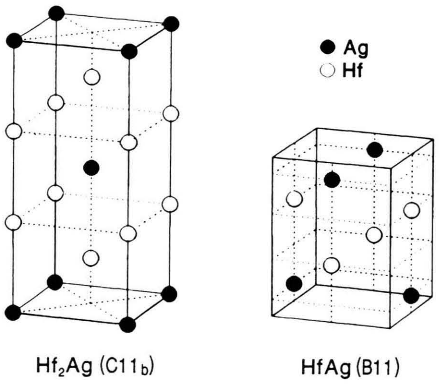

Fig. 1. The unit cells of Hf_2Ag and HfAg.

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* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23-28, 1995.

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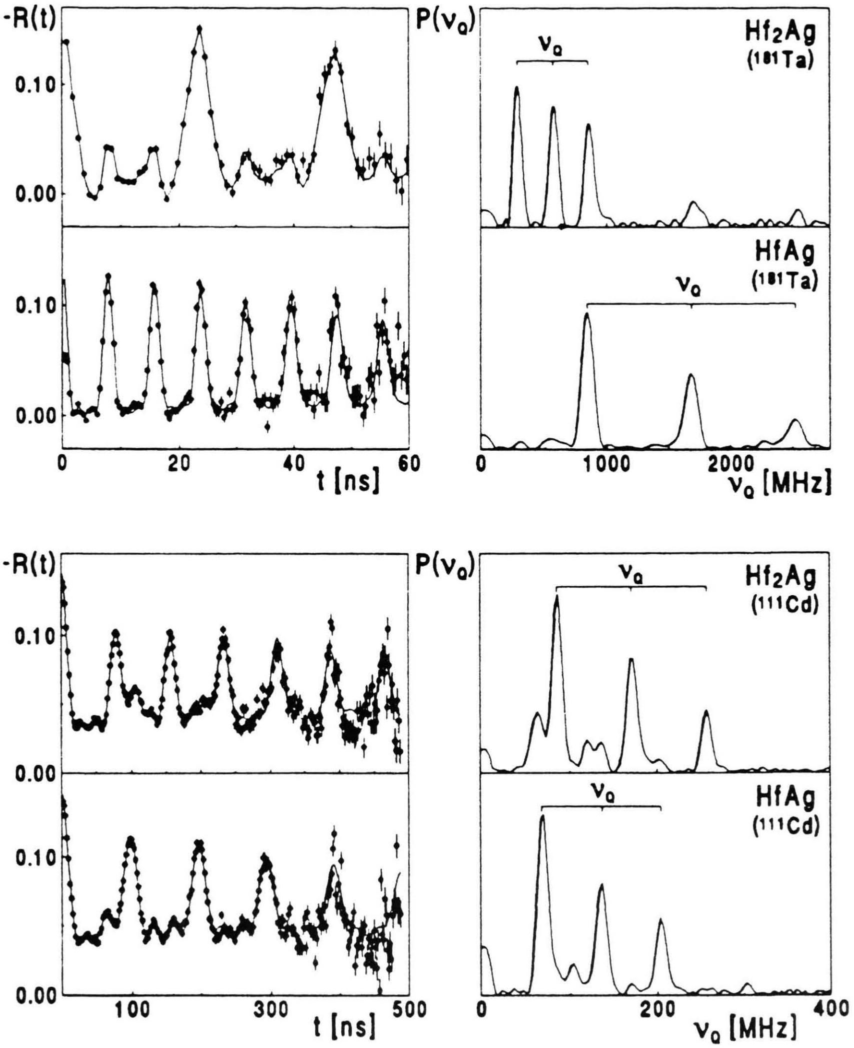

Fig. 2. Room temperature PAC spectra (with corresponding Fourier transforms) for ^{181}Ta and ^{111}Cd in Hf$_2$Ag and HfAg compounds.

2. Experimental details and data analysis

The HfAg and Hf$_2$Ag samples were prepared by argon arc melting followed by appropriate annealing in sealed and evacuated quartz tubes. The powder X-ray analysis confirmed the $B11$ structure of the HfAg sample and the $C11_b$ structure of the Hf$_2$Ag sample with some admixture of the HfAg phase. The samples were neutron irradiated in order to produce ^{181}Hf or α-irradiated to produce the ^{111}In activity, and annealed to remove 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 and 482 keV. A four NaI(Tl) detector apparatus with time resolution of 3 ns was used for the PAC measurements with ^{111}Cd probes.

The room temperature PAC spectra of ^{181}Ta and ^{111}Cd probes in HfAg and Hf$_2$Ag and their Fourier transforms are presented in Figure 2.

The perturbation factor

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

least squares fitted to the experimental PAC spectra, yielded the values of quadrupole frequencies ν_Q and asymmetry parameters η. Both HfAg and Hf$_2$Ag samples showed evidence of nonrandom orientation of the crystallites, and the PAC data had to be fitted with free s_{2n} parameters.

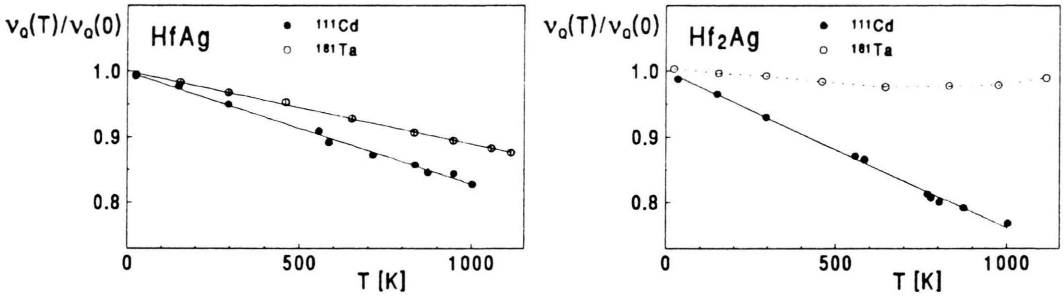

Fig. 3. The temperature dependence of quadrupole interaction frequencies for ^{181}Ta and ^{111}Cd in Hf_2Ag and HfAg samples.

Table 1. The ^{181}Ta and ^{111}Cd in HfAg and Hf_2Ag quadrupole interaction parameters: fraction f [%] of probe nuclei, quadrupole frequency $\nu_Q(295\ K)$ [MHz], asymmetry parameter η, slope a $[10^{-4}K^{-1}]$ of the temperature dependence $\nu_Q(T)$, the experimental room temperature value of the EFG V_{zz} $[10^{18}Vcm^{-2}]$ and the electronic enhancement factor $\alpha = | V_{zz}^{exp}/V_{zz}^{ion} |$.

Comp.	Probe	f	ν_Q	η	a	V_{zz}	α
HfAg	^{181}Ta	100	843(3)	0	1.11(2)	1.388(5)	0.70 - 0.82
	^{111}Cd	100	68(1)	0	1.73(5)	0.340(5)	0.23 - 0.41
Hf_2Ag	^{181}Ta	80(3)	285(1)	0		0.469(2)	0.20 - 0.37
	^{111}Cd	76(3)	86(1)	0	2.39(6)	0.428(5)	0.15 - 0.68

3. Results

The quadrupole interaction parameters of ^{181}Ta and ^{111}Cd in HfAg and Hf_2Ag are collected in Table 1.

For the HfAg sample a unique ν_Q = 843(3) MHz for ^{181}Ta and 68(1) MHz for ^{111}Cd and $\eta = 0$ were obtained, reflecting the existence of one axially symmetric 2(c) probe site in the $B11$ structure of the investigated sample.

The PAC patterns for the Hf_2Ag sample exhibit two components connected with $f_1 \approx 80\%$ and $f_2 \approx 20\%$ fractions of probes, each of them exposed to the well defined axially symmetric EFG. The corresponding quadrupole frequencies are for ^{181}Ta : ν_{Q1} = 285(1) MHz and ν_{Q2} = 840(8) MHz and for ^{111}Cd: ν_{Q1} = 86(1) MHz and ν_{Q2} = 68(1) MHz. The 285 MHz component is attributed to the ^{181}Ta probes situated in 4(e) Hf-sites of $C11_b$-type Hf_2Ag phase. The 86 MHz quadrupole frequency can be attributed to substitutional ^{111}Cd probe location either in 4(e) Hf-sites or in 2(a) Ag-sites of the Hf_2Ag crystal lattice. The four times smaller fractions of 840 MHz for ^{181}Ta and 68 MHz for ^{111}Cd are interpreted as due to the HfAg additional phase in the sample detected by X-ray analysis.

The temperature dependence of the quadrupole frequencies measured in HfAg and Hf_2Ag phases with ^{181}Ta and ^{111}Cd is shown in Figure 3. For HfAg a linear temperature dependence is observed for both probe nuclei. Also for ^{111}Cd probes in Hf_2Ag the ν_Q follows a linear T dependence. The solid lines in Fig. 3 represent fits of

$$\nu_Q(T) = \nu_Q(0)\,(1 - a\,T) \qquad (2)$$

to the data. The values of the slope parameter a are included in Table 1. For ^{181}Ta in Hf_2Ag, however, only extremely small temperature changes of ν_Q are observed and can not be fitted either with a linear T or with a $T^{3/2}$ dependence.

4. Discussion and Conclusions

Using the quadrupole moment value of the 247 keV state in ^{111}Cd (Q = 0.83(13) b) [2] and of the 482 keV state of ^{181}Ta (Q = 2.36 b) [3], the experimental values of the EFG at the impurity nuclei were computed from the measured quadrupole interaction frequencies and collected in Table 1. The room temperature value of the EFG at the Ta probe nuclei in HfAg is $1.388(5)\times10^{18}$ Vcm^{-2} while at the Cd probe it is four times smaller, being equal to $0.340(5)\times10^{18}$ Vcm^{-2}.

The $0.469(2)\times10^{18}$ Vcm^{-2} EFG value measured at ^{181}Ta in Hf_2Ag is similar to that observed in Hf_2Pd and Zr_2Pd [4] compounds, but is much larger than that reported for Zr_2Cu [5] and Hf_2Cu [6] isotypic compounds at the same probe. The EFG of $0.428(5)\times10^{18}$ Vcm^{-2} at Cd in Hf_2Ag has value similar to that obtained for the Ta probe.

Although the ^{111}Cd probe location is not unambigous, the measured fractions of ^{181}Ta and ^{111}Cd (both of $\approx 20\%$) in the additional HfAg phase of the Hf$_2$Ag sample, argue rather for the Cd impurity being located in substitutional 4(e) Hf-sites in the Hf$_2$Ag compound. An additional hint can also be the smaller charge difference between Hf and In ions than that between Ag and In ions and the fact that In has the same covalent radius as Hf.

The Cd and Ta probes as impurities in Hf$_2$Ag and HfAg differ in some obvious way which should affect the EFG. The ionic radii of Cd^{+2} (0.97 Å) and Ta^{+5} (0.68 Å) differ from each other and from those of the host Ag^{+1} (1.13 Å) and Hf^{+4} (0.82 Å) ions. Thus the host lattice must be subject to different local distortions due to different size mismatch of both impurities. Also a charge screening of the two impurities would be quite dissimilar because Cd^{+2} or Ta^{+5} impurity ions have different charges with respect to the lattice. The magnitude of the EFG ought to be affected by these impurity differences. These effects can also play a role in producing the difference in the temperature dependence of the EFG measured at different probes.

The total EFG V_{zz} is usually written as the sum of the ionic EFG $(1-\gamma_\infty)V_{zz}^{\text{lat}}$ and the electronic EFG V_{zz}^{el}:

$$V_{zz} = (1-\gamma_\infty)V_{zz}^{\text{lat}} + V_{zz}^{\text{el}}. \qquad (3)$$

The ionic contribution is easily determined from the lattice sum calculation of V_{zz}^{lat} and the tabulated Sternheimer correction factors $(1-\gamma_\infty)$ [7]. The electronic EFG V_{zz}^{el} can be calculated if both sign and magnitude of the total EFG have been measured. Since the sign of the EFG was not determined, the ratio

$$\alpha = |\, V_{zz}^{\text{exp}}/V_{zz}^{\text{ion}} \,| \qquad (4)$$

is introduced as a measure of the electronic contribution to the EFG. In numerous metallic hosts the electronic EFG is strongly correlated to the ionic contribution:

$$V_{zz}^{\text{el}} = -K\,(1-\gamma_\infty)\,V_{zz}^{\text{lat}};\ K = 2-5. \qquad (5)$$

For systems, which fit into this correlation, the electronic enhancement factor α, related to the K so that $\alpha = |\ 1-K\ |$, should be of the order 1÷4. Some transition metal probe-host combinations, however, show larger enhancements in the values of K. The magnitude of the local contribution to the EFG at transition element impurites should be proportional to the occupation of the d-states of the impurity which depends on the density of states of the host. Krusch and Forker observed that the metal probes of the second half of the transition series experience a large enhancement in the EFG's when alloyed with the transition metal hosts of the first half of this series [8]. There are no conspicuously large enhancement factors in the observed EFG's for the transition metal probes of the first half (Hf and Ta) of the transition series, whereas for a normal probe like Cd in Ti, Hf or Zr hosts, the V_{zz}^{el} is negligible [9].

The values of the electronic enhancement factor α for EFG at Ta and Cd probes in HfAg and Hf$_2$Ag compounds are listed in Table 1. In the α range calculations the uncertainties of the structural data [1] were included and in the case of Cd also both possible probe locations were taken into account. In spite of that, the possible α values in each case do not reach the range compatible with the universal correlation. The resulting low contribution of the electronic EFG in the systems studied is evident.

For most pure and impurity systems a $T^{3/2}$ dependence of EFG was found [10] and was understood as originating mainly from lattice vibrations and thermal lattice expansion [11]. There are, however, cases where a $T^{3/2}$ dependence is not observed [4, 12]. The deviations are not limited to transition metals, showing that they do not arise entirely from the local d-contributions. It is particularly interesting to investigate the temperature variation of the EFG for matrices which violate the universal correlation.

The present results of the EFG temperature dependence at ^{181}Ta and ^{111}Cd in Hf$_2$Ag and HfAg compounds (presented in Fig. 3 and Table 1) show that these systems do not follow a $T^{3/2}$ dependence. For both probes the linear behaviour of the EFG with temperature is observed in HfAg, and also for the ^{111}Cd probe in Hf$_2$Ag. However, for the Hf probe in Hf$_2$Ag the EFG follows neither a linear T nor a $T^{3/2}$ dependence. A similar EFG(T) behaviour was observed at ^{181}Ta in Hf$_2$Pd and Zr$_2$Pd, isotypic $C11_b$ compounds [4], but the temperature variation of the 285 MHz quadrupole frequency measured in Hf$_2$Ag is very weak. The slope is about 10 times smaller then that found in Hf$_2$Pd and Zr$_2$Pd.

A strong divergence of the temperature dependence between the Cd and Ta impurity in HfAg and Hf$_2$Ag is evident. The Cd probe exhibits in both compounds stronger EFG changes. The thermally induced repopulation of the d-states of different spatial symmetries at the Fermi level could account for dissimilar temperature dependences. A similar effect can result, however, from temperature changes in the s-electron contribution to the screening.

Acknowledgements

The authors would like to express their appreciation to Dr. A. Bajorek for X-ray analysis of the samples.

Work supported by the State Committee for Scientific Research (Grant No. 2P302 132 07).

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