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The nuclear quadrupole interaction of ^{181}Ta in the intermetallic compound Hf_2Ni

M Manasijević, S Koički, B Cekić and N Ivanović

Institute of Nuclear Sciences Vinča, Physics Laboratory, PO Box 522, 11001 Belgrade, Yugoslavia

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Abstract. The time-differential perturbed angular correlation technique has been used to study the electric field gradient at ^{181}Ta impurities in the intermetallic compound Hf_2Ni . The results of the measurements show the presence of a single nuclear quadrupole interaction. At room temperature the frequency of the interaction is $\omega_Q = 92(1) \text{ Mrad s}^{-1}$. The electric field gradient V_{zz} and asymmetry parameter η exhibit a pronounced temperature dependence in a range varying from 78 to 1125 K.

1. Introduction

In contrast with the nuclear quadrupole interaction (NQI) of probe nuclei in pure non-cubic metals which has been studied extensively, much less information has been collected in the case of NQIs in ordered intermetallic compounds. However, in comparison with pure metals, intermetallic compounds offer the probe ion much more parameters within the same lattice, such as different but well defined crystallographic surroundings consisting of different atoms at different interatomic distances as well as the opportunity to sense the degree of order and phase transition in the lattice. Hence, this large group of metallic systems opens up new ways of varying certain parameters which characterize the metallic state and thus contribute to a better understanding of the electric field gradients (EFGs) in metals.

In recent years, a few papers have been published [1–5] devoted to the time-differential perturbed angular correlation (TDPAC) investigation of NQIs in ordered intermetallic compounds of the transition metal Hf. It was shown that the EFG reveals interesting properties in these compounds. The general impression is that the origin and the magnitude of the EFG in these cases have no simple explanation and that no simple temperature law for the temperature dependence of the NQI parameters can be established. All this work stimulated further investigations of the NQIs in these intermetallic systems.

In this paper a TDPAC measurement of the NQI of ^{181}Ta in the intermetallic compound Hf_2Ni is reported. A pronounced temperature dependence of the EFG is observed and the results are considered in close connection with the crystalline structure of this compound.

2. Experimental details

Samples of Hf_2Ni were prepared by melting appropriate amounts of the constituent elements in an induction furnace under a very pure argon stream. The single-phase BCT CuAl_2 (C16)-type structure of the compound was confirmed by a powder x-ray diffractogram. Lattice constants were found to be $a = 6.479(3) \text{ \AA}$ and $c = 5.271(3) \text{ \AA}$.

The main feature of the $\text{Hf}_2\text{Ni}(\text{C16})$ -type structure appears to be two sets of mutual orthogonal planes with a dense packing of hexagons (honeycomb structure) with Hf atoms, parallel to the (110) and ($\bar{1}\bar{1}0$) planes, respectively. The hexagons of the different sets are fully interlocking. The Ni atoms are situated in the channels parallel to the c axis, which are formed by this interlocking honeycomb structure. A fuller account of the crystallographic study of binary compounds with the $\text{CuAl}_2(\text{C16})$ -type structure was reported by Havinga *et al* [6].

The 133–482 keV γ cascade of ^{181}Ta is populated by the β decay of the parent ^{181}Hf nucleus. ^{181}Hf was produced by neutron irradiating the Hf_2Ni sample in an evacuated quartz ampoule in a reactor. In order to repair neutron irradiation damage the sample was annealed at 900°C for 5 d.

The TDPAC measurements of the 133–482 keV γ cascade of the ^{181}Ta nuclei were performed with a conventional two- BaF_2 -detectors coincidence set-up. The coincidence spectra between γ -rays in the cascade were recorded with a time resolution better than 0.5 ns FWHM. Details about the high-resolution TDPAC set-up have been described elsewhere [5]. Source temperatures below room temperature were obtained with a simple liquid-nitrogen cryostat. For measurements above room temperature the source was heated in a low-scattering electric furnace.

3. Data analysis and results

From the coincidence spectra measured at the angles $\vartheta = 90^\circ$ and $\vartheta = 180^\circ$ and after subtraction of a linear background, the experimental perturbation function $R(t)$ was calculated as

$$R(t) = 2 \frac{N(180^\circ) - N(90^\circ)}{N(180^\circ) + 2N(90^\circ)}. \quad (1)$$

The ratio $R(t)$ was fitted using a theoretical function $A_2 G_2(t)$, where A_2 is the unperturbed angular correlation coefficient and $G_2(t)$ is a perturbation factor for a randomly oriented static NQI in a polycrystalline sample. The NQI of the quadrupole moment Q of the $I = \frac{5}{2}$ level in ^{181}Ta with an EFG V_{zz} results in the hyperfine splitting of the level into three sublevels, and the perturbation factor has the form

$$G_2(t) = a_{20} + \sum_{n=1}^3 a_{2n} \exp\left(-\frac{(\omega_n \tau_R)^2}{2}\right) \exp(-\delta \omega_n t) \cos(\omega_n t). \quad (2)$$

The transition energies $\hbar\omega_n$ between sublevels depend on the quadrupole frequency ω_Q :

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \quad (3)$$

and the asymmetry parameter η , whereas the coefficients a_{20} and a_{2n} are functions of the asymmetry parameter η only [3]. In addition to the modulation of the perturbation function (equation (1)) a reduction in and damping of the oscillation amplitudes $a_{2n}(\eta)$ are present in realistic spectra. These effects are introduced through a finite time resolution τ_R of the TDPAC apparatus and a more or less broad distribution δ of the effective EFG caused by small irregularities in the atomic positions in the lattice. The first and second exponential

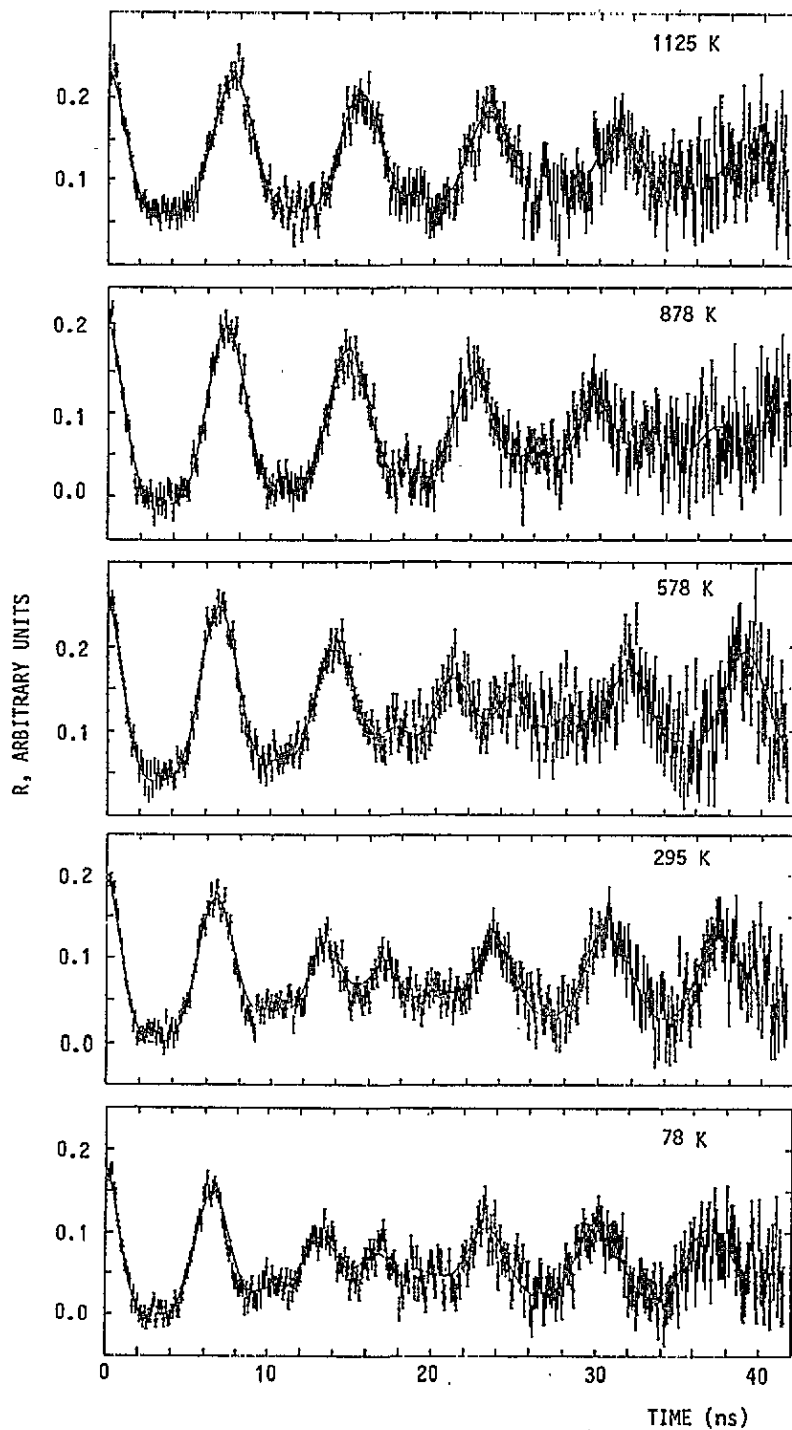


Figure 1. TDPAC spectra of ^{181}Ta in the intermetallic compound Hf_2Ni at different temperatures: —, theoretical fit.

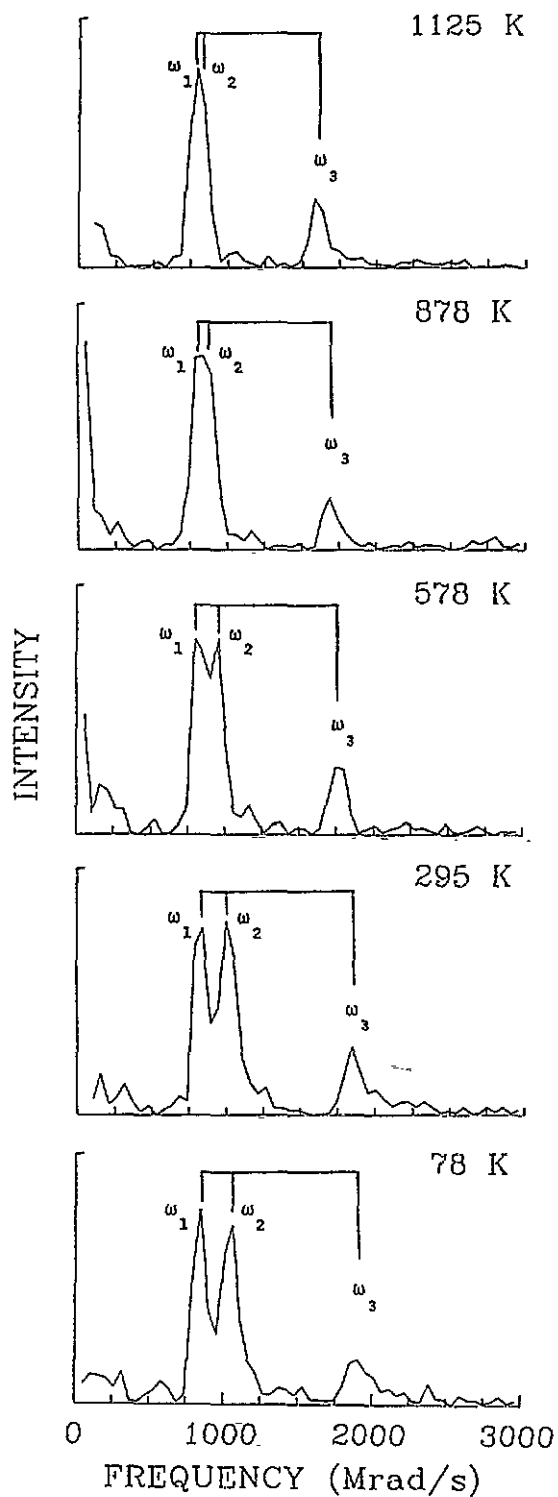


Figure 2. Fourier-transformed TDPAC spectra of the intermetallic compound Hf_2Ni in arbitrary units at different temperatures.

terms in the sum in equation (2) account for the finite time resolution of the coincidence system and the Lorentzian frequency distribution of the NQI, respectively.

The experimentally observed TDPAC spectra of ^{181}Ta at five different temperatures for Hf_2Ni , together with the fitted curves $A_2G_2(t)$, are shown in figure 1. The important feature to be noted in the fitted spectra and corresponding Fourier transforms (figure 2) is that the sample exhibits a single quadrupole interaction with little damping and a large asymmetry parameter η . As is seen from the frequency spectra (figure 2), very well defined peaks were observed. Consequently, we were able to extract a sharp value of the asymmetry parameter η , considerably improving starting conditions for the final fit. The results of the least-squares analysis of the measured TDPAC spectra are summarized in table 1. The quadrupole frequency ω_Q , as can be seen from figure 3, varies strongly with temperature and does not follow exactly the $T^{3/2}$ dependence observed for almost all pure non-cubic metals. We suggest a linear $\omega_Q(T)$ dependence with the slope equal to $1.67(2) \times 10^{-4} \text{ K}^{-1}$. However, although a similar linear $\omega_Q(T)$ dependence is known to exist in some intermetallic compounds with a $\text{CuAl}_2(\text{C16})$ -type structure [4, 7, 8], more experimental points are needed in the low-temperature region to clarify the situation for Hf_2Ni . Using the known value of the quadrupole moment $Q = +2.36(5) \times 10^{-24} \text{ cm}^2$ [9] for the $I = \frac{5}{2}$ state in ^{181}Ta , the effective EFG V_{zz} (equation (3)) acting on the Ta nuclei at the Hf site is found to be $10.3(1) \times 10^{17} \text{ V cm}^{-2}$ at 295 K in Hf_2Ni . All the other results for the EFG at different temperatures are given in table 1. Further, the asymmetry parameter η of the EFG indicates a considerable temperature variation, too (figure 4). The observed $\eta(T)$ dependence means that the ratio of the transition frequencies ω_1 and ω_2 from equation (2) depends on temperature (as can be seen from figure 2). This suggests that the symmetry of the measured EFG strongly depends on the local environment of the probe atoms and is not merely a function of the bulk properties of Hf_2Ni . Hence, as can be seen from figure 1, as the temperature is changed, not only does the interaction frequency ω_Q change, but also so does the shape of the TDPAC pattern. These changes in the pattern are attributed mostly to a change in the asymmetry parameter η with temperature, since the lineshape parameter δ remain relatively small and essentially constant over the entire temperature range (table 1).

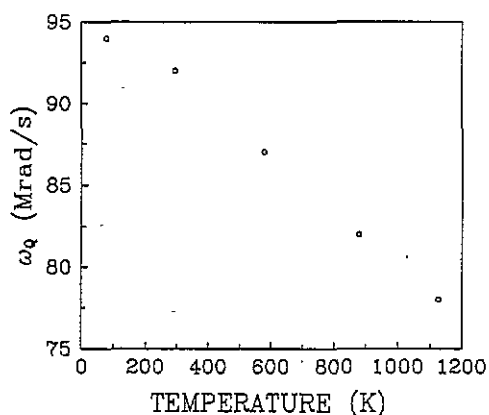


Figure 3. Quadrupole frequency ω_Q derived from the TDPAC spectra for ^{181}Ta impurities in the intermetallic compound Hf_2Ni as a function of temperature.

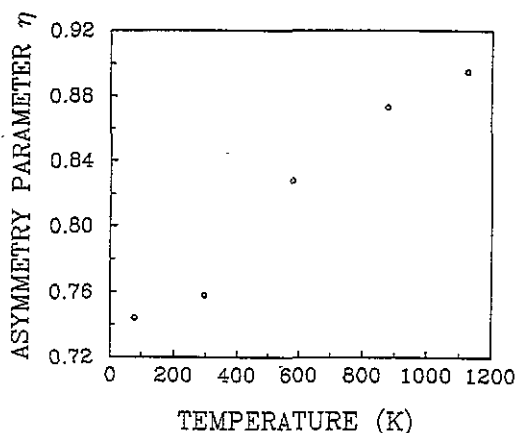


Figure 4. Asymmetry parameter η plotted as a function of temperature for ^{181}Ta impurities in the intermetallic compound Hf_2Ni .

Table 1. The EQI parameters for ^{181}Ta impurities in the intermetallic compound Hf_2Ni .

T (K)	ω_Q (Mrad s $^{-1}$)	η	δ	V_{zz} (10^{17} V cm $^{-2}$)
78	94(1)	0.744(4)	0.034(3)	10.5(1)
295	92(1)	0.758(3)	0.034(2)	10.3(1)
578	87(1)	0.828(3)	0.023(2)	9.7(1)
878	82(1)	0.873(4)	0.019(2)	9.1(1)
1125	78(1)	0.895(6)	0.016(3)	8.7(1)

4. Discussion

Within the experimental uncertainty all spin rotation patterns and corresponding frequency spectra (figures 1 and 2, respectively) show that the ^{181}Ta probe occupies a unique site in the Hf_2Ni lattice experiencing a largely asymmetric EFG. The observed value of the EFG at room temperature is in good agreement with previous briefly reported measurements [1, 4].

Traditionally, the effective EFG $V_{zz}(\text{eff})$ at an impurity nuclear site in a host non-cubic conducting materials is usually considered to arise from firstly a lattice EFG $V_{zz}(\text{latt})$ due to the positively charged ions multiplied by the Sternheimer enhancement factor $1 - \gamma_\infty$ and secondly an electronic contribution $V_{zz}(\text{el})$ caused by the non-spherical charge density of the conduction electrons. Therefore, the effective EFG is usually written as [8]

$$V_{zz}(\text{eff}) = V_{zz}(\text{ion}) + V_{zz}(\text{el}) \quad (4)$$

where

$$V_{zz}(\text{ion}) = (1 - \gamma_\infty)V_{zz}(\text{latt}). \quad (4a)$$

The ionic contribution to the EFG (equation (4a)) can be calculated in a straightforward manner by a lattice sum calculation. The second contribution to the EFG due to the electrons in the conduction band is far from fully understood and the term $V_{zz}(\text{el})$ (equation (4)) is very difficult to evaluate theoretically, since it requires a detailed knowledge of the structure and the population of the conduction band.

Thus the ionic EFG at the Hf site in the Hf_2Ni intermetallic compound can be calculated by summing over the individual contributions of all lattice ions. Since there are two different components forming the investigated compound, two separate point lattice sums need to be calculated: one for the sublattice formed by the Hf atoms, and one for the sublattice of the Ni atoms. Further, it is very well known that the effective EFG and corresponding asymmetry parameter η depend strongly upon the effective charge of the ions in each sublattice. For pure metals this charge is usually set equal to the nominal valence of the ion forming the lattice, but in the present case the problem is somewhat more complicated and requires additional considerations. It is found [6] that for the intermetallic compounds with $\text{CuAl}_2(\text{C16})$ -type structure the average number of valence electrons per atom is significantly different from the nominal valence of the ions forming the lattice and also markedly dependent on the c/a lattice ratio. For the Hf_2Ni compound the average number of valence electrons per atom is $n = \frac{8}{3}$ [6]. This value was obtained by taking one third of the total number of outer electrons of the atoms per formula AB_2 , with the restriction that, if A is a transition metal with m outer electrons, its contribution to n is negative and equal to $(m - 10)/3$ [6]. Moreover, from the reported value of the average number n of valence electrons per atom for Hf_2Ni , it can be concluded that the effective charge of the Ni atoms is zero for the Ni

sublattice and thus no contribution to the lattice EFG exists. Using these assumptions in the lattice sum calculations and the value for $^{181}\text{Ta}^{5+}$ of $1 - \gamma_\infty = +62$ [10], it is found that the ionic contribution to the effective EFG (equation (4a)) is about $-18.8 \times 10^{17} \text{ V cm}^{-2}$ at 295 K. The corresponding asymmetry parameter η is about 0.47. Although numerical values of the point-charge-derived EFG and η cannot be trusted completely owing to the lack of exact knowledge of the effective ionic charges involved, the electronic contribution to the effective EFG can be calculated using equation (4) and following the empirical rule of Raghavan *et al* [11] that the electronic EFG is larger than the ionic EFG and usually has the opposite sign [8]. In this way, it is found that the electronic contribution to the effective EFG is about $+29.1 \times 10^{17} \text{ V cm}^{-2}$. This value is in good agreement with previously reported lattice sum calculations in a similar intermetallic compounds with the CuAl_2 (C16)-type structure [4, 8]. However, the asymmetry parameter η derived from lattice sum calculations is about half that experimentally observed. Although this discrepancy was observed and briefly reported previously [4], no explanation for this can be given at present.

Therefore, within the framework of the model (equation (4)), the experimentally observed EFG in the intermetallic compound Hf_2Ni is compared with the prediction of the lattice sum model in order to deduce the magnitude of the electronic EFG. As is seen, the electronic contribution makes a major contribution to the effective EFG. The absolute value of the ionic EFG (equation (4a)), and hence also of the electronic EFG, is uncertain to the extent to which assumptions enter into equation (4) and lattice sum calculations. However, the observed gross temperature variation in the effective EFG and the corresponding asymmetry parameter η may be considered as an additional argument for the idea of a predominantly local origin of the effective EFG in Hf_2Ni . Obviously, a fuller understanding of the origin and of the observed behaviour of the EFG may be expected when the exact theoretical calculations of the electron density (near the probe nucleus at Hf site) in the considered intermetallic compound become available.

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