

Evidence for a hybridization-induced electric quadrupole interaction in the intermetallic compound Hf_2Fe

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The time-differential perturbed angular correlation technique has been used to study the temperature dependence of the electric-field gradient at ^{181}Ta impurity in the Hf_2Fe intermetallic compound. The results of the measurements show the presence of two independent electric quadrupole interactions, compatible with the crystalline structure of the compound. At room temperature the frequencies of the interactions are $\omega_{Q1}=21(1)$ Mrad/s and $\omega_{Q2}=212(1)$ Mrad/s. The low-frequency interaction exhibits unusual temperature dependence characterized by a pronounced maximum at about 450 K. Specific-heat measurements of the Hf_2Fe compound were performed and they revealed a similar maximum of C_p at the same temperature value. An explanation of the origin and magnitude of the electric quadrupole interactions is proposed, assuming that at the $48f$ -crystallographic site the local electronic contribution to the electric-field gradients is mainly determined by the tantalum-iron hybridization.

INTRODUCTION

In the past several years the intermetallic compound Hf_2Fe has been the subject of many investigations, mostly concerning the absorption of hydrogen by this compound. Recently, however, two groups of investigators (Refs. 1–3) have revealed interesting properties of the electric quadrupole interaction (EQI) at the ^{181}Ta probe ion in the Hf_2Fe lattice and observed through the time-differential perturbed angular correlation method (TDPAC). It was shown that electric-field gradients (EFG's) at the two crystallographically nonequivalent sites of Hf ions in the Hf_2Fe compound differ substantially in their magnitude and temperature dependence. Furthermore, the value of the EFG at one of the sites exhibits an unusually large value. All this work stimulated further investigations of the EQI in this system (Ref. 4).

In this paper we present a high-resolution TDPAC study of the Hf_2Fe system performed with a time resolution of the coincidence system better than 0.5 ns at the 482–133-keV gamma energies of the ^{181}Ta , together with specific-heat C_p measurements on the Hf_2Fe compound. These data, together with recent experimental and theoretical investigations of this and related systems, permitted us to consider an explanation of EQI anomalies observed in this intermetallic compound.

EXPERIMENT

Source preparation

Samples of the Hf_2Fe compound were prepared by melting component materials in an induction furnace in a pure Ar atmosphere. The single-phase cubic structure of the Ti_2Ni type was confirmed by a powder X-ray diffractogram. The unit cell of Hf_2Fe has 96 atoms and

dimensions $a = 12.0333(3)$ Å. The space group is $Fd\bar{3}m$. Thirty-two atoms of Fe are in the $32e$ positions, while 64 atoms of Hf are in the $16c$ and $48f$ positions. A more detailed account of the crystallographic study of the Hf_2Fe compound was published elsewhere (Ref. 2).

The 133–482-keV gamma cascade of ^{181}Ta is populated by the β decay of the ^{181}Hf isotope. The ^{181}Hf isotope was activated by neutron irradiation in a reactor of the Hf_2Fe samples in an evacuated quartz ampoule. In order to repair neutron irradiation damages, the sample was annealed at 900 °C for five days. According to previous investigations (Refs. 1–4), post-irradiation annealing of the source ensures a significantly improved structure of the TDPAC pattern.

The irradiated and annealed sample was crushed and a small piece (of several milligrams) was used as a source of the measurements. Hence, the source in these measurements had a negligible self-absorption of gamma rays.

Experimental setup

The TDPAC measurements of the 482–133-keV gamma cascade of the ^{181}Ta probe were carried out in a planar setup of two BaF_2 detectors (35 mm $\Phi \times 40$ mm and 35 mm $\Phi \times 10$ mm) coupled to XP2020Q photomultiplier tubes. Since high-frequency EQI's were involved (Refs. 2–4) a high-resolution coincidence setup had to be used. In order to ensure good time resolution, only the first nine dynodes of the XP2020Q photomultiplier tube were used. The positive timing signal was derived from the seventh dynode and immediately followed by a new ORTEC VT-120 fast amplifier (rise time < 1 ns, gain ≈ 200) before feeding a standard constant-fraction discriminator. This combination decreased substantially the current load on the photomultiplier tubes and made the detectors extremely suitable for TDPAC measure-

ments where long run and high-counting-rate conditions are typical. The time resolution of the coincidence system was not degraded by the insertion of fast amplifiers and was easily maintained at the level of better than 0.5 ns throughout the experiment. The high- and low-temperature TDPAC measurements were performed with a low gamma ray scattering furnace and liquid-nitrogen dewar structure, respectively.

Measurements and results

The experimental perturbation function $R(t)$ was derived

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

The function $R(t)$ was fitted using a theoretical $G_2(t)$ perturbation factor for the static EQI in a polycrystalline sample. The perturbation factor $G_2(t)$ for the probe ion with intermediate spin level $I = \frac{5}{2}$ is written as

$$G_2(t) = a_{20} + \sum_{n=1}^3 a_{2n} \cos \omega_n t, \quad (2)$$

where frequencies ω_n are dependent on the EFG and its asymmetry parameter η , whereas the coefficients a_{20} and a_{2n} are functions of the asymmetry parameter η only.

In addition to the modulation of the perturbation function, a damping of the oscillation amplitudes $a_{2n}(\eta)$ is usually present in realistic spectra. It is introduced through a finite time resolution τ_R for the TDPAC apparatus and a more-or-less broad distribution δ of the EFG caused by lattice imperfections and charge impurities. The perturbation factor becomes

$$G_2(t) = a_{20} + \sum_{n=0}^3 a_{2n} \exp \left[-\frac{(\omega_n \tau_R)^2}{2} \right] \times \exp(-\delta \omega_n t) \cos(\omega_n t). \quad (3)$$

In this expression the first and second exponential terms account for the finite time resolution of the coincidence system and the Lorentzian frequency distribution of the EQI, respectively.

In some crystals atoms, of one element may occupy several inequivalent crystallographic sites. Each site is then characterized by its population fraction f_i and by corresponding EQI parameters ω_{Qi} , η_i and δ_i . The measured perturbation function $R(t)$ is written as a linear combination of perturbing factors:

$$R(t) = A_2 \sum_{i=1}^n f_i G_{2i}(t), \quad (4)$$

where A_2 is unperturbed angular correlation coefficient, $i = 1, n$ is the number of different sites of probe ions in a

crystal lattice, and $G_2(t)$ is defined by Eq. (3). It should be emphasized that the number of different sites in a particular case is usually chosen on the basis of the *a priori* available information from crystallographic data of the specimen and the Fourier analysis of the measured TDPAC spectra. In the present investigation, the measurements of the TDPAC spectra of the Hf_2Fe compound were performed at 20 temperatures in the range from 77 to 1200 K.

Figure 1 shows typical Fourier transforms of the measured TDPAC spectra at different temperatures (only extreme temperatures are displayed). As is seen from the Fourier spectra, very-well-defined peaks were observed for the high-frequency EQI. Consequently, we were able to extract a sharp value of the asymmetry parameter η for the $48f$ site, considerably improving starting conditions for the fit. Furthermore, due to the good time resolution of the TDPAC system, even ω_3 frequency peaks of this interaction were clearly extracted, reaching 4300 Mrad/s at low temperature.

In the final fit, all our TDPAC spectra Hf were completely described with the theoretical curve defined in expression (4) assuming Hf ions occupy only two different sites. The corresponding EQI parameters for these two sites determined from the nonlinear least-squares fits of the spectra are listed in Table I.

Figure 2 shows the typical spin rotation spectrum $R(t)$ together with the decomposition into its component fit curves. As can be seen, the detailed structure shown in the time-domain spectrum [Fig. 2(a)] is fitted excellently with two very different static EQI's. The main contribution to the precession pattern is due to the high-frequency component [Fig. 2(b)], identified with the $48f$ site of Hf atoms. This interaction is easily extracted from the data and provides EQI parameters of a high degree of precision. The second, $16c$ -site EQI [Fig. 2(c)] is much more difficult to investigate, due mainly to a relatively small fraction of Hf atoms at this site and particularly to a relatively weak strength of interaction, leading to a lack

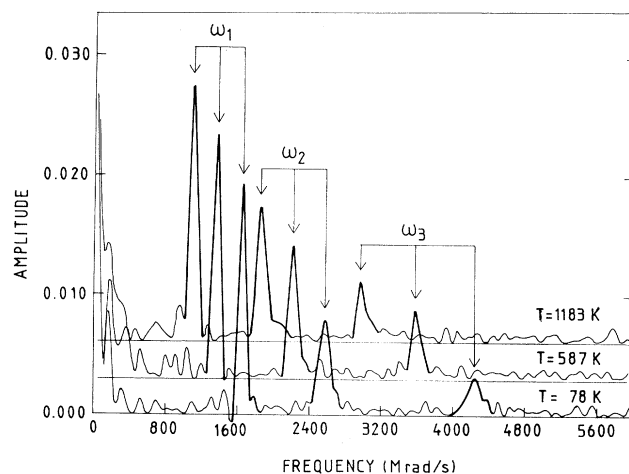


FIG. 1. Fourier-transformed TDPAC spectra of Hf_2Fe in arbitrary units, at different temperatures.

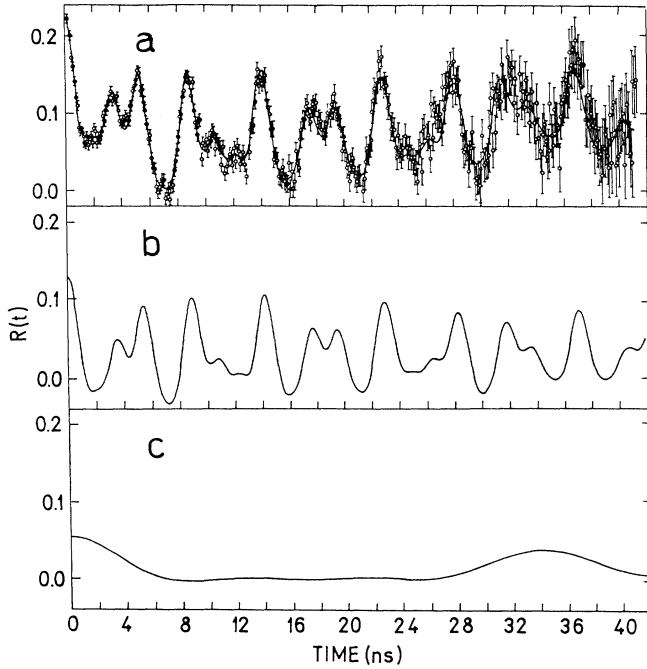


FIG. 2. TDPAC spectrum of ^{181}Ta in Hf_2Fe at 587 K. The solid line is the theoretical fit (a). The high- and low-frequency components of the perturbation curve from (a) are shown with (b) and (c), respectively.

of characteristic modulation details in the available time interval of about 40 ns. But in the present investigation it is resolved considerably better than in previous experiments (Refs. 1, 3, and 4). Least-squares fitting of this interaction was done both with fixed ($\eta=0$) and with a free asymmetry parameter η . Considerably better fits of the

measured spectra were obtained with the parameter η set free (yielding values of η of about 0.23).

The temperature dependence of the EFG at the 48f crystallographic site is displayed in Fig. 3 (upper curve). It is observed that it is remarkably linear. Figure 4 presents the temperature dependence of the corresponding parameter η . The EQI at the 16c crystallographic site and its temperature dependence (Fig. 3, lower curve) will be discussed in more detail in the following section.

In order to investigate further the temperature behavior of the Hf_2Fe compound, we performed the specific-heat C_p study, using differential-temperature-analysis (DTA) measurements in the temperature range from 300 to 780 K. A Perkin-Elmer DCS-2 system with Al sample holders and a standard 30-mg sapphire sample were used. The heating velocity was 10 K/min. The mass of the measured Hf_2Fe sample was 80 mg. The specific heat C_p was evaluated as

$$C_p = C_{ps} \frac{W_s D_s}{W D}, \quad (5)$$

where W_s and W are masses, and D_s and D are signals obtained with the sapphire standard and the Hf_2Fe sample, respectively. C_{ps} are tabulated values at corresponding temperatures. Corrections for the specific heat of Al holders were also made. The base line was extremely flat and stable throughout the measurements. Consequently, the maximum estimated error in the measurements was below 5%.

The specific heat C_p of the Hf_2Fe compound as a function of temperature is presented in Fig. 5. It is observed that the C_p curve reveals a broad maximum at about 450 K similar to that exhibited by the strength of the EQI at the 16c crystallographic site (Fig. 3).

TABLE I. The EQI parameters of ^{181}Ta nuclei at two different positions occupied by Hf ions in Hf_2Fe .

T (K)	48f position				16c position	
	ω_Q (Mrad/s)	η	δ	V_{zz} (10^{17} V/cm 2)	ω_Q (Mrad/s)	V_{zz} (10^{17} V/cm 2)
78	223(1)	0.497(1)	0.012(1)	23.4(1)	11(1)	1.1(1)
295	212(1)	0.475(1)	0.011(1)	22.3(1)	21(1)	2.2(1)
369	205(1)	0.461(2)	0.009(1)	21.5(1)	26(1)	2.7(1)
422	200(1)	0.454(2)	0.009(1)	21.0(1)	30(1)	3.1(1)
474	197(1)	0.447(2)	0.012(1)	20.7(1)	31(1)	3.2(1)
518	195(1)	0.439(2)	0.010(1)	20.5(1)	30(1)	3.1(1)
557	191(1)	0.437(2)	0.007(1)	20.1(1)	30(1)	3.1(1)
626	188(1)	0.427(2)	0.010(1)	19.8(1)	29(1)	3.0(1)
673	185(1)	0.422(2)	0.010(1)	19.4(1)	29(1)	3.0(1)
722	183(1)	0.420(2)	0.007(1)	19.2(1)	27(1)	2.8(1)
775	182(1)	0.410(2)	0.006(1)	19.1(1)	26(1)	2.7(1)
825	178(1)	0.418(2)	0.008(1)	18.7(1)	25(1)	2.6(1)
848	175(1)	0.413(2)	0.008(1)	18.4(1)	26(1)	2.7(1)
931	172(1)	0.403(2)	0.010(1)	18.1(1)	24(1)	2.5(1)
974	169(1)	0.402(2)	0.008(1)	17.7(1)	22(1)	2.3(1)
1025	167(1)	0.399(2)	0.008(1)	17.5(1)	21(1)	2.2(1)
1075	164(1)	0.399(2)	0.012(1)	17.2(1)	20(1)	2.1(1)
1129	161(1)	0.395(2)	0.012(1)	16.9(1)	18(1)	1.8(1)
1168	158(1)	0.399(2)	0.011(1)	16.6(1)	18(1)	1.8(1)
1237	156(1)	0.385(3)	0.019(1)	16.4(1)	16(1)	1.6(1)

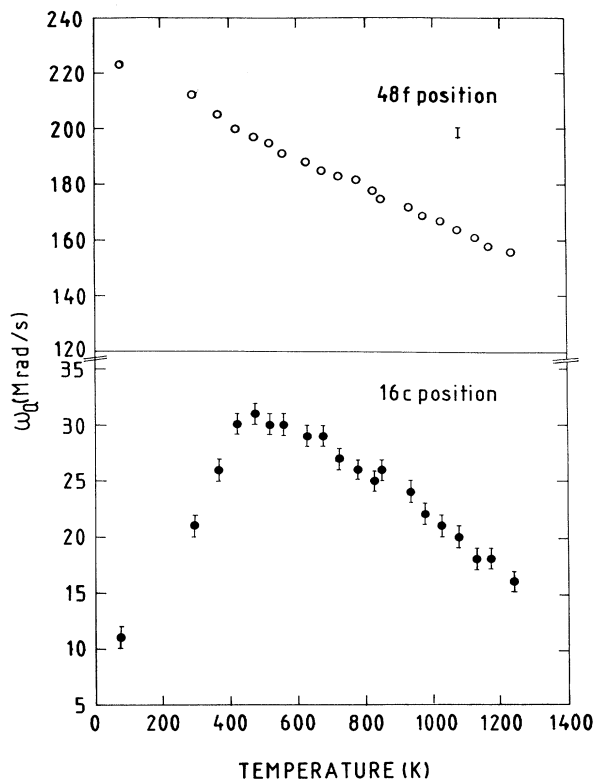


FIG. 3. Quadrupole frequency ω_Q derived from the TDPAC spectra for two different ^{181}Ta positions in Hf_2Fe as a function of temperature.

DISCUSSION

Traditionally, the total EFG in noncubic metals is written as the sum of the ionic EFG $(1-\gamma_\infty)V_{zz}(\text{latt})$ and the electronic EFG $V_{zz}(\text{el})$. Furthermore, a correlation between the ionic and electronic parts of the total EFG was observed and often referred as “universal correla-

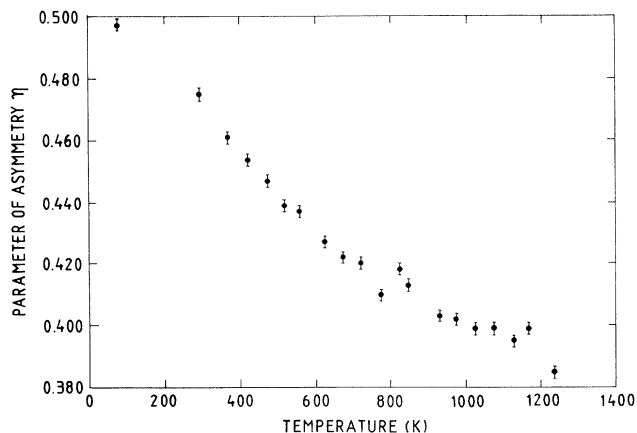


FIG. 4. Asymmetry parameter η plotted as a function of temperature for the $48f$ ^{181}Ta position in Hf_2Fe .

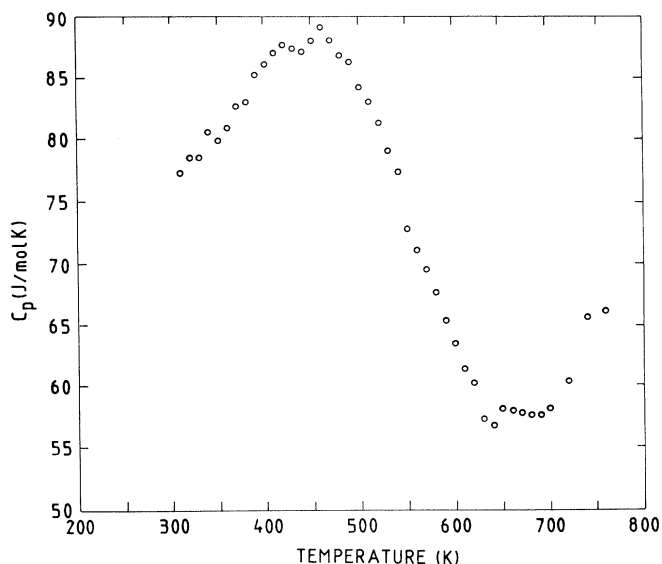


FIG. 5. Temperature dependence of the specific heat C_p for Hf_2Fe .

tion.” In a large number of impurity-host combinations the electronic contribution is approximately 2–5 times larger than the ionic EFG and has the opposite sign. Usually, the ratio

$$\alpha = \frac{V_{zz}}{(1-\gamma_\infty)V_{zz}(\text{latt})} \quad (6)$$

is introduced as a measure of the electronic contribution to the total EFG V_{zz} , where $V_{zz}(\text{latt})$ is the ionic contribution determined from a lattice sum calculation and γ_∞ is the tabulated Sternheimer correction factor.

However, a considerable number of cases have been reported where either the sign or the magnitude of the electronic EFG was incompatible with this correlation. It is remarkable that in all these cases the host metal or the probe atom belongs to a transition element series. The most-pronounced deviations from the correlation have been observed for the $5d$ impurity in the $3d$ -host combination, where the electronic EFG is roughly 50 times larger than the ionic EFG (Ref. 5).

The striking feature of the EFG observed in the Hf_2Fe compound is its high value, probably the largest ever observed for a ^{181}Ta probe ion in any metallic medium. On the basis of the crystalline structure of the cubic Hf_2Fe lattice, the point-charge lattice sum calculations of the ionic EFG at the $48f$ and $16c$ sites are reported to be (at room temperature) 4.2×10^{14} and 3.0×10^{14} V/cm², respectively (Ref. 1). The electronic enhancement factor α is then derived to be 85 for the $48f$ crystallographic site and 12 for the $16c$ site. Although numerical values of these calculated EFG’s cannot be trusted completely due to the lack of knowledge of the effective ionic charges involved, the large value of the factor α at the $48f$ site in comparison to that at the $16c$ site strongly suggests that unclosed d shells of the Ta and Fe ions are responsible for the enhancement. In the following discussion we present

arguments to support the contention that Ta-Fe hybridization in the Hf_2Fe compound is likely to be the mechanism explaining the large electronic enhancement factor.

The 48f crystallographic site

The pure Hf_2Fe intermetallic compound is known to be a Pauli paramagnet. However, it was observed that when this compound is gradually being filled up with hydrogen (Refs. 6,7,8), the magnetic moment at the Fe atoms reappears. This particular characteristic of the Hf_2Fe compound has been thoroughly investigated since this discovery. Buschow and van Diepen (Ref. 6) were the first to propose that in the pure Hf_2Fe intermetallic compound, hybridization between iron and hafnium atoms takes place, which is presumably destroyed by the strong Hf—H bonds when hydrogen is being introduced into the lattice. More direct evidence of these phenomena was provided by Teisseron, Vulliet, and Schlappbach⁷ in their photoelectron study of the pure and hydrogenated Hf_2Fe compound. These authors found that in pure Hf_2Fe , the iron 2*p* core level is by far less asymmetric than in pure iron, indicating a weak partial density of iron states at the Fermi level E_F , owing to a lowering of the iron 3*d* conduction states below E_F . Nevertheless, the iron 3*d* electrons in this compound still behave as valence electrons in the sense that they hybridize with wave functions of the neighboring atoms (3*d* electrons of Fe with 5*d* and 6*s* electrons of Hf).

Recently, Dederichs *et al.*⁹ reported their *ab initio* calculations of EFG on a series of 3*d* and 4*sp* impurities (titanium to arsenic) in a copper lattice. The new approach in their calculations was that the *d* electrons are explicitly treated as valence electrons, as opposed to previous calculations where they have been considered as core electrons, and entered the results only via the Sternheimer factor. These authors found that, despite the fact that the Cu *d* band was considered full and located well below the Fermi energy, the number of *d* electrons in copper changes due to the hybridization with neighboring atoms. For instance, the *d* electrons of the transition-metal impurities form bonding and antibonding hybrids with the Cu *d* states. The antibonding states are mostly unoccupied for the impurities at the beginning of the series and are slowly filling up when progressing in the *d* series. Thus, as a consequence of hybridization, unoccupied antibonding states with strong Cu *d* admixture may be formed. Dederichs *et al.* found that these highly directional “*d*-hole states” gave rise to the major part of the EFG at the impurity.

The basic physical mechanism revealed by the calculation in Ref. 9 is likely to be responsible for the exceptionally large value of the EFG observed at the tantalum probe nuclei at the 48*f* site in Hf_2Fe (EFG-48*f*). Although tantalum ions have a somewhat smaller metallic radius than hafnium ions, one may assume that at this crystallographic site the Ta-Fe hybridization still takes place. In this picture it is expected that the *d*-*d* contribution to the formation of EFG-48*f* dominates over the *p*-*p* contribution, since tantalum ions belong to the beginning of the 5*d* transition series. As a consequence, the unoccu-

pled antibonding hybrid states are formed, which greatly enhance the EFG at the Ta-probe nuclei. We may note that a similar effect was both calculated and experimentally observed in the case of a vanadium impurity in a copper lattice (Ref. 9), whereas we may remember that vanadium is the 3*d* analogue of tantalum.

The role of *d*-*d* hybridization was also considered by Riegel *et al.*¹⁰ as the mechanism underlying the formation of the magnetic moment on Fe, Co, and Ni atoms in many transition-metal hosts. As was noticed by these authors, magnetic moments have never been observed in case of Ta hosts, which indicates the presence of some additional mechanism of suppression of the ferromagnetic part of the *d*-*d* interaction when Ta and Fe ions are involved. This observation is in agreement with the absence of any static or time-dependent magnetic interaction in the Hf_2Fe compound when observed by the TDPAC technique.

An additional argument in favor of the proposed hybridization mechanism of formation of the EFG-48*f* may be found in the temperature dependence of the strength of the EQI at the 48*f* site (Fig. 3, upper part). It is observed that $\omega_Q(T)$ follows nearly the straight line (possibly with a minor departure) in the whole broad temperature range where C_p exhibits its major change, which is presumably connected with a phase transition in the Hf_2Fe lattice. This insensitivity of the EFG-48*f* to a rearrangement in the broader lattice may be considered an indication of the importance of a local bonding (Ta-Fe hybridization) to the formation of the EFG-48*f*. We may note that the asymmetry parameter η of this interaction does not exhibit either an observable departure from its smooth flow in the region of the phase transition (Fig. 4). The same conclusion is valid when considering the temperature behavior of the parameter δ , measuring the width of the EFG-48*f* distribution (Table I). It is seen that the EFG-48*f* remains exceptionally *sharp* in the whole temperature range 78–1237 K, suggesting great stability of the bond participating in its formation.

The 16c crystallographic site

The magnitude of the EFG at this site (EFG-16*c*) is about one order of magnitude smaller than at the 48*f* site and thus approaches the “normal” values at the ¹⁸¹Ta probe in most metallic systems. This fact suggests that the EFG-16*c* is induced the usual way, e.g., through the balanced intervention of a larger cluster of electrons and ions surrounding the probe ion.

However, the temperature dependence of the hyperfine interaction at the 16*c* site exhibits a clear anomaly with respect to that at the 48*f* site and to most metallic systems investigated up to now. Since the experimental investigation of the 16*c*-site interaction is fraught with considerable difficulties, we present here some details of the analysis of our data. First, we use the fact that the high-frequency 48*f*-interaction is characterized by many features and after the fitting procedure can be precisely subtracted from the measured pattern. Thus the TDPAC spectra of the 16*c* interaction alone at different temperatures can be deduced. Analysis of these spectra shows

that at temperatures above about 500 K this interaction can be described well as a static EQI with a linear, negative-temperature dependence. Below this temperature, however, the pattern progressively loses its structure, and at 78 K reduces to a simple decay of the anisotropy down to a constant value. In order to test the physical nature of this behavior, we tried to fit 16c patterns at low temperatures by assuming (i) an exponential decay of $G_2(t)$, which would account for an eventual relaxation process of the Ta ion in the lattice (Refs. 11 and 12) and (ii) a very strong, technically unresolved static EQI, which could account for a transition of the system to a state with very high EFG at lower temperatures. In either case no satisfactory fit to experimental data was possible. We therefore conclude that the static EQI prevails in the whole temperature range investigated, the transition toward lower temperatures being accompanied by a decrease in magnitude of the EFG-16c and a considerable increase of the width of its distribution. The corresponding temperature dependence is presented in Fig. 3 (lower curve).

It can be noted that the observed temperature dependence of the EFG-16c exhibits great similarity to the temperature dependence of the specific heat C_p of the Hf_2Fe compound (Fig. 5). Both curves show broad maxima centered at about the same temperature of 450 K. It is therefore tempting to associate the EFG-16c behavior with changes in the Hf_2Fe lattice as reflected through the C_p singularity. At present, however, the nature of the observed phase transition in the ordered Hf_2Fe compound is not yet established. It may be connected with a minor ionic rearrangement in the vicinity of the 16c site or to changes in the long-range order of the whole intermetallic compound. From the present EQI measurements it follows that at lower temperatures the electrical environment of the 16c site becomes more spherically symmetric and less sharply defined. This interpretation does not contradict the high point symmetry of the 16c crystallographic site.

Great sensitivity of the EFG-16c to changes in a broader lattice, as evidenced through its temperature dependence, may be regarded as independent evidence that the EFG-16c site is induced by a larger number of charged species in the lattice. The same conclusion followed from consideration of the magnitude of this EFG. The unusual temperature dependence of the EFG-16c seems then to be induced by the particular dynamics of this intermetallic compound. As was pointed out before, the EFG-48f shows a quite different behavior; its magnitude greatly surpasses the usual values and it exhibits provocative insensitivity to the phase transition in the lat-

tice. All this seems to be consistent with the idea of a strictly local origin of the EFG at this site, presumably induced by an iron-tantalum hybridization.

From the present EQI study in the Hf_2Fe compound, there is no evidence that the magnitude of EFG-16c exhibits an anomaly with respect to EFG's observed at the Ta probe ion in the majority of other metallic systems. Hence there are no grounds to seek an explanation of the EFG by invoking other mechanism, such as hybridization. However, the presence of Ta-Fe hybridization at the 16c site cannot be excluded, provided that, due to symmetry reasons, its overall effect leads to a relatively low value of the EFG.

CONCLUSION

It is demonstrated that the Hf_2Fe intermetallic compound presents the case where the TDPAC method can provide high-quality data on the EQI of the ^{181}Ta probe nucleus. These data reveal the rich phenomenology associated with this metallic system. Full understanding of this intermetallic compound will require further experimental and theoretical investigations, particularly the accomplishment of corresponding energy-band calculations.

Up to recently, the EQI's in intermetallic compounds have been little investigated. The reason is probably that the increased inherent complexity of the interactions in these systems has not been matched by a corresponding analytical power of traditional TDPAC techniques. The introduction of BaF_2 detectors has greatly improved this situation and has rendered these interesting metallic systems more amenable to a more thorough study by PAC. In comparison, for instance, to alloys, intermetallic compounds offer the probe ion more parameters within the same lattice, such as different but well-defined crystallographic surroundings consisting of different atomic species at different interatomic distances as well as the opportunity to sense the degree of order and phase transition in the lattice. Together with recent progress in precision energy-band calculations, this approach seems to offer an interesting field of investigation.

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