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# Electronic structure and electric field gradient calculations for $\text{Hf}_2\text{Fe}$ intermetallic compounds

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**Abstract.** Using the first-principles full-potential linear muffin-tin orbital method in the atomic sphere approximation, we have calculated the electronic structure of the intermetallic compound  $\text{Hf}_2\text{Fe}$ , and evaluated the electric field gradients (EFGs) at all of the three inequivalent positions (two Hf and one Fe) in its lattice. The main results extracted from the experimental investigations, concerning the different magnitudes and origins of the EFGs at inequivalent Hf sites, are correctly reproduced. The possible mechanisms of formation of the EFGs at these sites are analysed and discussed.

## 1. Introduction

The intermetallic compound  $\text{Hf}_2\text{Fe}$  has attracted much attention recently, mostly because of its ability to absorb a large amount of hydrogen. It was observed that this absorption changes the magnetic properties of the compound  $\text{Hf}_2\text{FeH}_x$ , from Pauli paramagnetism for  $x = 0$ , to Langevin paramagnetism for  $x = 1.5$ , to ferromagnetism for  $x \geq 2.5$  [1–3].

These interesting properties stimulated further investigations of the pure compound  $\text{Hf}_2\text{Fe}$ , such as measurements of the electric quadrupole interaction (EQI). These measurements were performed by two experimental groups [4,5]. Both of them used the time-differential perturbed-angular-correlation (TDPAC) method, with the  $^{181}\text{Ta}$  as a probe atom, in order to determine the EFGs at inequivalent Hf positions, and to explain the microscopic properties in the vicinity of the nuclei. Their investigations revealed that the EFGs at two inequivalent Hf sites differ substantially in magnitudes and temperature dependences, thus indicating the existence of different mechanisms of formation of these EFGs. The existence of high-quality experimental data concerning the EFG problem in the compound  $\text{Hf}_2\text{Fe}$  and the inadequacy of the attempts at their interpretation [4], as well as a lack of any band-structure calculations for  $\text{Hf}_2\text{Fe}$ , stimulated us to treat this compound theoretically, and to try to elucidate the origin of the differences observed experimentally for the EFGs at two inequivalent Hf sites.

In this paper we have presented the electronic structure of the intermetallic compound  $\text{Hf}_2\text{Fe}$ , obtained in a fully self-consistent manner using the full-potential (FP) linear muffin-tin orbital (LMTO) atomic sphere approximation (ASA) method. As a central feature of the paper, we have evaluated EFGs at all of the three inequivalent positions in the  $\text{Hf}_2\text{Fe}$  lattice, and offered an explanation of their origins. Besides the magnitudes of the principal components of the EFG tensors and the corresponding asymmetry parameters, we have also obtained the signs and orientations of the EFGs. On the basis of decomposition of the principal component of the EFG tensor, we have established the orbital types of the electrons which participate in the formation of each EFG separately, and discussed the results obtained.

The paper is organized as follows. In section 2, after a brief description of the theoretical method and the technical details of the calculations, we have presented the electronic structure of the compound  $\text{Hf}_2\text{Fe}$ . In section 3, the results for the EFGs at all of the inequivalent sites in this compound are given. In section 4, our results for the EFGs are compared with the experimental ones, and the interpretation of the results obtained has been given.

## 2. Details of the calculations and electronic structure

The electronic structure and EFG tensors for the compound  $\text{Hf}_2\text{Fe}$  have been calculated by use of the first-principles version of the FP-LMTO ASA method [6]. This is a simpler version of the complete FP-LMTO method [7], in which non-muffin-tin (MT) corrections are taken into account, using the angular momentum representation for all relevant quantities within MT spheres, as well as in the interstitial region.

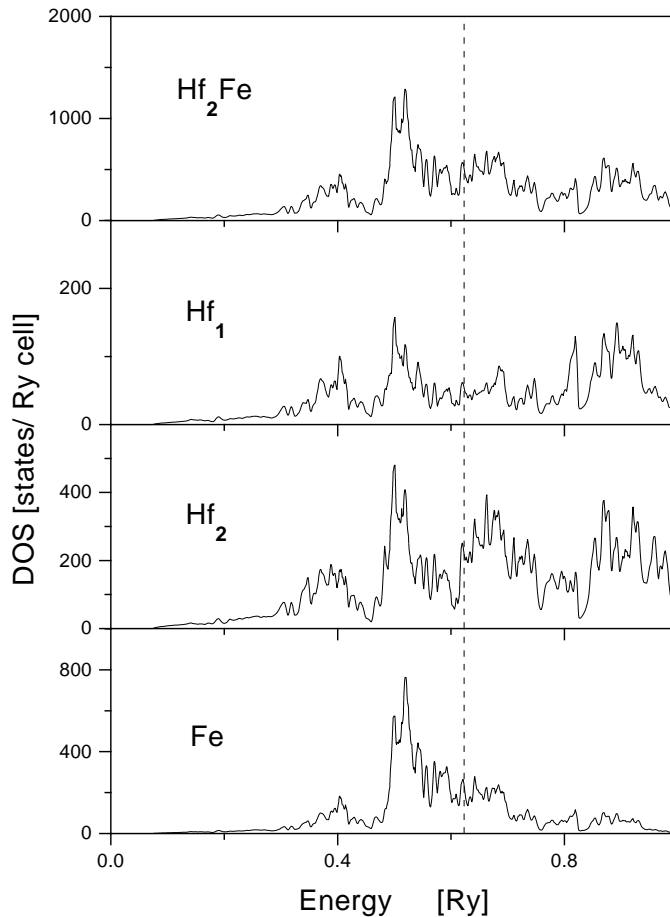
The FP-LMTO ASA method is based on density-functional theory in its local-density approximation (LDA). In this formalism, crystal space is filled with overlapping Wigner–Seitz (WS) spheres centred at each atomic position, so that the total volume of the WS spheres equals the volume of the crystal. Within the spheres, the electronic wave function is given as a linear combination of numerical solutions of the Schrödinger equation. This equation is solved without using any shape approximation for the crystal potential. The same holds for the electronic charge density, which is expressed as an angular momentum expansion inside the WS sphere:  $\rho(\vec{r}) = \sum_{l,m} \rho_{lm}(r) i^l Y_l^m(\hat{r})$ , where the  $Y_l^m$  are spherical harmonics. Consequently, although the original meaning of the ASA is the application of the two approximations, the spherical approximation for the potential inside the atomic sphere and the lack of an interstitial space, only the later is implied in the FP-LMTO ASA method. This could also be seen from reference [7], where the complete FP-LMTO method is described. All of the formulae given there, concerning the construction of the muffin-tin orbitals, Hamiltonian, and overlap matrix, are valid in the ASA case also, provided that all of the contributions coming from the interstitial space are omitted. Due to the finite overlap of the atomic spheres, and the lack of the interstitial region in the ASA approximation, the non-spherical potential and charge density are not as accurate as those in generic full-potential methods. But the FP-LMTO ASA method has the advantage of a high computational efficiency and speed. We have shown that its accuracy is quite appropriate for the precise calculation of the EFG [8,9].

The intermetallic compound  $\text{Hf}_2\text{Fe}$  crystallizes in the  $\text{Ti}_2\text{Ni}$ -type structure. It has a cubic symmetry, with a space group  $Fd\bar{3}m$ . The primitive cell of this compound consists of 24 atoms. That is, there are four Hf atoms at 16c crystallographic sites (in Wyckoff notation) with the point symmetry  $\bar{3}m$ , twelve Hf atoms at 48f positions ( $mm$ ), and eight Fe atoms at 32e positions ( $3m$ ):

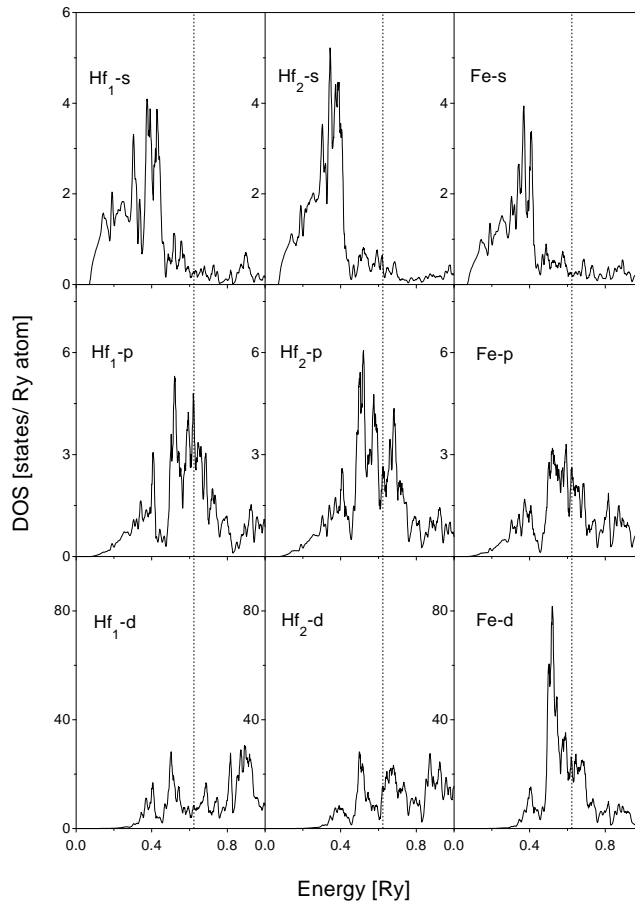
$$\begin{aligned}
 16\text{c-Hf (Hf}_1\text{)}: & \quad (0, 0, 0); (1/4, 1/4, 0); (1/4, 0, 1/4); (0, 1/4, 1/4) \\
 48\text{f-Hf (Hf}_2\text{)}: & \quad \pm (x, 1/8, 1/8); \pm(1/8, x, 1/8); \pm(1/8, 1/8, x); \\
 & \quad \pm (1/4 - x, 1/8, 1/8); \pm(1/8, 1/4 - x, 1/8); \pm(1/8, 1/8, 1/4 - x) \\
 32\text{e-Fe (Fe)}: & \quad \pm (y, y, y); \pm(y, 1/4 - y, 1/4 - y); \\
 & \quad \pm (1/4 - y, y, 1/4 - y); \pm(1/4 - y, 1/4 - y, y)
 \end{aligned}$$

while the primitive translations are  $(0, 1/2, 1/2)$ ,  $(1/2, 0, 1/2)$ ,  $(1/2, 1/2, 0)$ . For the parameters which define actual atomic positions we have used  $x = -0.1847$  and  $y = 0.2116$  [10]. All of the coordinates are given in units of the lattice constant  $a = 12.0333 \text{ \AA}$ , taken from the most recent experimental data [4]. In order to simplify the notation, we have denoted the 16c-Hf, 48f-Hf, and 32e-Fe sites as  $\text{Hf}_1$ ,  $\text{Hf}_2$ , and Fe sites respectively.

The band-structure calculation itself is characterized by the following technical details. All hafnium and iron electronic states have been partitioned into the valence and core ones. The valence 6s, 6p, 5d, and 4f states were included in basis set for Hf, as well as the 4s, 4p, and 3d states for Fe. The importance of the treatment of 4f Hf states in a self-consistent manner has been discussed in our previous paper [9]. Core states were considered as atomic-like. A one- $\kappa$  basis set has been used, with fixed tail energy  $\kappa^2 = -0.25$  Ryd, placed approximately at the centre of the occupied part of the valence panel. All of the calculations were scalar relativistic, including mass-velocity and Darwin terms, without spin-orbit interaction. Integration in  $\bar{k}$ -space was performed using the improved tetrahedron method [11] with a mesh of 72 points in the irreducible wedge of the first Brillouin zone. The local-density approximation of von Barth and Hedin [12] was employed in describing exchange and correlation effects. Finally, the WS sphere radii have been chosen in such a way as to make the boundary potential values not very different for different types of atom, and taking into account the fact that the overlap between spheres must not be too large. We found that with the choice of 3.272 au for the  $\text{Hf}_1$  sphere radius, 3.200 for the  $\text{Hf}_2$  sphere radius, and 2.671 au for the Fe sphere radius, the above-mentioned conditions were satisfied.



**Figure 1.** The total and projected FP-LMTO ASA electronic densities of states for the compound  $\text{Hf}_2\text{Fe}$ . The dashed line indicates the Fermi level.



**Figure 2.** The *l*-decomposed FP-LMTO ASA electronic densities of states for Hf<sub>1</sub>, Hf<sub>2</sub>, and Fe sites in the compound Hf<sub>2</sub>Fe. The dashed line indicates the Fermi level.

The resulting electronic structure of the intermetallic compound Hf<sub>2</sub>Fe has been obtained in a fully self-consistent manner, with the energy precision criterion set at  $10^{-6}$  Ryd, by performing spin-restricted FP-LMTO ASA calculations. The main features of the electronic structure obtained can be seen from the total and projected densities of states (DOS and PDOS), which are presented in figures 1 and 2. According to these pictures, it is obvious that the compound Hf<sub>2</sub>Fe is a typical metal, having a large DOS at the Fermi level. The bands which are responsible for the electrical conductivity are mainly centred at the Fe and Hf<sub>2</sub> sites. The contributions from these sites to the DOS at the Fermi level are equal to 275.2 and 225.4 states Ryd<sup>-1</sup>/cell respectively, compared to 57.1 states Ryd<sup>-1</sup>/cell originating from the Hf<sub>1</sub> site. However, if these contributions are given per atom (not per cell), the differences between them become smaller (14.3, 18.8, and 34.4 states Ryd<sup>-1</sup>/atom for Hf<sub>1</sub>, Hf<sub>2</sub>, and Fe sites respectively).

More detailed information about the electronic structure can be extracted from the PDOS pictures (figure 2). It can be seen that the s states of all of the three inequivalent sites in the compound do not contribute significantly to the DOS in a region close to the Fermi level. As for the Hf<sub>1</sub> site, the contributions from the p and d states to the DOS at the Fermi level are

of the same order (5.5 and 8.0 states  $\text{Ryd}^{-1}/\text{atom}$  respectively). In the case of the  $Hf_2$  site, however, the situation is quite different. The contribution from the d states is much larger than that from the p states (15.2 versus 2.6 states  $\text{Ryd}^{-1}/\text{atom}$ ). This distinction between the two inequivalent Hf sites is accompanied by differences in the shapes of the PDOS curves, which are most pronounced for the d states. While for the  $Hf_1$  site the Fermi level falls into the region of the PDOS minimum, for the  $Hf_2$  site it passes through the beginning of the PDOS maximum, consisting of several peaks.

**Table 1.** Occupation numbers for  $Hf_1$ ,  $Hf_2$ , and Fe sites in the compound  $Hf_2Fe$ .

	s	p	d	f	g	Charge
$Hf_1$	0.772	0.706	2.755	13.84	0.066	+0.139
$Hf_2$	0.811	0.807	2.591	13.94	0.021	+0.170
Fe	0.595	0.557	6.378	0.089	0.057	-0.324

The occupation numbers and the charge transfer between the WS spheres centred on the inequivalent sites in the compound  $Hf_2Fe$  are given in table 1. The redistribution of the s electrons for both  $Hf_1$  and  $Hf_2$  atoms has occurred, filling up the p and d states mostly. The same effect is observed for Fe atoms also.

The f states of the Hf atoms are not displayed in figures 1 and 2, and not discussed above. Their position is far below the Fermi level, and they retained almost all of their own electrons (table 1). However, inclusion of the Hf 4f states into the FP-LMTO ASA basis set has a large effect on the EFG calculations, through their influence on the p and d states of Hf. This subject is discussed in our recent publication concerning the EFG calculations of the compound  $Hf_2Ni$  [9].

### 3. EFG calculations

The EFG tensor is defined as a second derivative of the electrostatic potential:

$$V_{ij} = \left. \frac{\partial^2 \Phi}{\partial x_i \partial x_j} \right|_{r=0} \quad \{x_i = x, y, z\} \quad (1)$$

evaluated at the position of the nucleus. Here  $V_{ij}$  is a symmetric, second-rank tensor with zero trace because of Laplace's equation  $\Delta \Phi = 0$ . Consequently, this tensor has only five independent components, and it can be diagonalized by rotating the coordinate system. The new coordinate system, whose principal axes are denoted as  $\{X, Y, Z\}$ , is usually chosen in such a way that  $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$ . The EFG tensor is then completely determined by its principal component  $V_{ZZ}$ , the asymmetry parameter  $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ , and the orientation of the principal-axis system. In two special cases, when the nucleus is placed in an environment with cubic or axial symmetry, the number of parameters describing the EFG tensor can be reduced. In the first case, the EFG tensor completely vanishes, and in the second one,  $\eta = 0$ , i.e.  $V_{XX} = V_{YY}$ . More details about this topic can be found in an extensive review article [13].

The electrostatic potential in (1) is generated by all of the charges in the crystal which interact with the observed nucleus. It can be written as a sum of the potential induced by the charges confined in the WS sphere, and the potential generated by the charges from the rest of the crystal. Consequently, the EFG tensor can be separated into the contribution originating from the valence electrons within the WS sphere, and the so-called lattice contribution. In our recent paper [9] the formulae for all of the components of the EFG tensor were presented,

for both of the above-mentioned contributions. On the basis of these formulae, after the self-consistent solution for the electronic structure has been reached under the conditions described in the previous section, we have calculated the EFG tensors for all of the three inequivalent sites in the compound  $\text{Hf}_2\text{Fe}$ . The following results have been obtained.

The lattice contribution to the EFG tensor can be neglected, because it participates at a level of less than 3% for all of the sites in the compound. This result is often obtained in the cases of the metallic systems, and can be explained by very efficient screening of the charges which are positioned outside the observed WS sphere. Thus, from now on, it will be considered that the EFG tensor consists of the contribution from the valence electrons only. The results for the EFG will be presented for each inequivalent site separately, in units of  $10^{17} \text{ V cm}^{-2}$ .

(a) *Hf<sub>1</sub> sites*

In the Cartesian coordinate system  $\{x, y, z\}$ , in which the positions of the atoms in the unit cell are given, all diagonal components of the EFG tensor are zero. This is the consequence of the fact that the  $\rho_{20}$ -component in the angular momentum expansion of the charge density vanishes due to the symmetry properties of the  $\text{Hf}_1$  site. Non-diagonal components are all non-zero, and have equal absolute values. Transforming the EFG tensor to the principal-axis system, we have obtained:  $V_{XX} = V_{YY} = +2.55$ , the main component  $V_{ZZ} = -5.1$ , and the asymmetry parameter  $\eta = 0$ . The possibility of decomposing the EFG values [9, 14] enables one to establish the individual contributions to the EFG coming from the s, p, d, or f electrons, and to reveal its origin. For  $\text{Hf}_1$  sites, we found that the contribution from the d electrons exceeds the contribution from the p electrons ( $-3.3$  versus  $-2.2$ ), while s and f electrons are of much less importance. As regards the orientation of the principal component  $V_{ZZ}$ , it is different for all of the  $\text{Hf}_1$  sites. Respecting the sequence in which the  $\text{Hf}_1$  atoms are positioned in the unit cell, the  $V_{ZZ}$ -components are parallel to the  $[1, 1, 1]$ ,  $[1, 1, \bar{1}]$ ,  $[1, \bar{1}, 1]$ , and  $[\bar{1}, 1, 1]$  directions respectively.

(b) *Hf<sub>2</sub> sites*

In the  $\{x, y, z\}$  coordinate system, the EFG tensor looks quite different to that for the  $\text{Hf}_1$  sites. All of the diagonal components of the tensor are non-zero, two of them being of equal magnitude, but half the size and with opposite sign compared to the third one. Besides them, there exists just one symmetrical pair of non-zero off-diagonal components. Their value is about an order of the magnitude greater than the largest diagonal component. The characteristics described determine the basic properties of the EFG in the principal-axis system. That is, after diagonalizing the EFG tensor we have obtained:  $V_{XX} = +1.0$ ,  $V_{YY} = +12.0$ ,  $V_{ZZ} = -13.0$ , and a large value of the asymmetry parameter  $\eta = 0.845$ . Decomposition of the principal component  $V_{ZZ}$  has shown that the largest contribution to the EFG came from 6p electrons ( $-11.2$ ), while the contributions from 5d and 4f electrons were  $-1.0$  and  $-0.8$  respectively. Thus, it can be said that 6p electrons practically dominate the EFG at  $\text{Hf}_2$  sites. Since inversion has no effect on the EFG tensor (which follows from the definition (1)), the sites connected by this symmetry operation have equal values for  $V_{ZZ}$  and  $\eta$ , as well as the same orientation of the principal axes. Other sites, although equivalent, may have differently oriented principal axes. Our calculations predict that the main components  $V_{ZZ}$  are parallel to the  $[0, 1, 1]$ ,  $[1, 0, 1]$ ,  $[1, 1, 0]$ ,  $[0, \bar{1}, 1]$ ,  $[\bar{1}, 0, 1]$ , and  $[\bar{1}, 1, 0]$  directions, for the sequence of  $\text{Hf}_2$  atoms given in the order in which they are positioned in the unit cell.

(c) *Fe sites*

For these sites, the EFG tensor has the same properties as that for  $\text{Hf}_1$  sites. Our calculations predict a value for the principal component  $V_{ZZ}$  which is close to zero ( $+0.3$ ), while the

asymmetry parameter is  $\eta = 0$ . Such a small value of  $V_{ZZ}$  is a result of cancellation of the contributions to the EFG from p electrons ( $-0.7$ ) and d electrons ( $+1.0$ ) of iron. Although the EFG at the Fe sites has not been measured in the experimental studies [4, 5] mentioned in the introduction, there exist experimental data from Mössbauer spectroscopy measurements [15], where the quadrupole splitting of  $0.46 \text{ mm s}^{-1}$  was derived. We have converted this splitting to the EFG using a value of  $0.16 \text{ b}$  [16] for the nuclear quadrupole moment of  $^{57}\text{Fe}$ . In that way, we have obtained  $V_{ZZ} = 2.7 \times 10^{17} \text{ V cm}^{-2}$  for the experimental value of the EFG at Fe sites in  $\text{Hf}_2\text{Fe}$ . For such small values of the EFG, the differences between the theoretical and experimental data are quite acceptable.

The results for the EFGs presented above are summarized in table 2.

**Table 2.** Decomposition of the calculated  $V_{ZZ}$ -values, in units of  $10^{17} \text{ V cm}^{-2}$ .

	s-d	p-p	d-d	p-f	f-f	$V_{ZZ}$	$\eta$
Hf <sub>1</sub>	0.1	-2.2	-3.3	0.0	0.3	-5.1	0
Hf <sub>2</sub>	0.0	-11.2	-1.0	0.0	-0.8	-13.0	0.845
Fe	0.0	-0.7	1.0	0.0	0.0	0.3	0

#### 4. Comparison with the experiment and discussion

The electric quadrupole interaction (EQI) in  $\text{Hf}_2\text{Fe}$  was recently investigated by two experimental groups [4, 5]. They have been using the TDPAC technique to study the temperature dependence of the EFG at  $^{181}\text{Ta}$  probes at the two inequivalent Hf positions in that compound. The basic conclusions extracted from these investigations could be briefly summarized as follows.

Firstly, a large difference between the magnitudes of the EFGs at Hf<sub>1</sub> and Hf<sub>2</sub> sites has been observed. A Moscow group [5] has obtained  $V_{ZZ} = 1.05 \pm 0.2$ , keeping the value  $\eta = 0$  fixed for Hf<sub>1</sub> sites, compared to values of  $V_{ZZ} = 19.1 \pm 0.1$  and  $\eta = 0.505(7)$  for Hf<sub>2</sub> sites. A Belgrade group [4], using a spectrometer with better time resolution in their measurements, has obtained  $V_{ZZ} = 1.1(1)$  and  $\eta = 0$  for Hf<sub>1</sub> sites, and  $V_{ZZ} = 23.4(1)$  and  $\eta = 0.497(1)$  for Hf<sub>2</sub> sites. The above results for  $V_{ZZ}$  are given in units of  $10^{17} \text{ V cm}^{-2}$ , and have been taken from the measurements performed at the lowest temperature of  $T = 78 \text{ K}$ . The signs for the EQIs have not been determined.

Secondly, it has been found that the EFGs at two inequivalent Hf positions exhibit different temperature dependencies. The EFG at Hf<sub>1</sub> sites is characterized by the increase of its magnitude with raising of the temperature to  $\sim 500 \text{ K}$ , where a pronounced maximum exists. After that, the EFG gradually decreases following a linear dependence. At the same time, the magnitude of the EFG at Hf<sub>2</sub> sites decreases linearly over the whole temperature range, having a maximum value at the lowest temperature. The experimental differences described indicate the existence of different mechanisms of formation of the EFG at two inequivalent Hf sites in the intermetallic compound  $\text{Hf}_2\text{Fe}$ .

The experimental EFG measurements for  $^{181}\text{Ta}$  impurities in  $\text{Hf}_2\text{Fe}$  should reflect the situation occurring at Hf atoms in the same compound, at least in a qualitative manner. Our theoretical EFG calculations, performed for Hf (not Ta) atoms, confirmed that assumption. Although a direct quantitative comparison of our results with the experimental ones is not possible, we have found that the basic conclusions extracted from the experiment are valid in the case of the pure  $\text{Hf}_2\text{Fe}$  compound (without Ta impurities) also. That is, the properties of the



EFGs at Hf atoms at inequivalent Hf positions are qualitatively the same as the experimentally observed ones at  $^{181}\text{Ta}$  impurities at Hf sites in the compound  $\text{Hf}_2\text{Fe}$ . This could be clearly seen from the table 2. Our calculations predicted a large difference (not as large as in the experiment though) between the magnitudes of the EFGs at inequivalent Hf sites, as well as different origins of these EFGs, indicated by the fundamentally different decompositions of their values. These facts were established from the TDPAC measurements also. In addition, we have predicted the signs and orientations of the EFGs, which are quantities that have not been determined from the experiment.

In spite of the lack of relevant theoretical calculations, the authors of reference [4] tried to give some explanation for the origin of the EFGs at Hf sites in  $\text{Hf}_2\text{Fe}$ . They suggested that the EFG at  $\text{Hf}_1$  sites is induced the usual way, ‘... through the balanced intervention of a larger cluster of electrons and ions surrounding the probe ion’. This suggestion was based on their statement that the measured value of the EFG at  $\text{Hf}_1$  sites ‘... approaches the ‘normal’ value at the  $^{181}\text{Ta}$  probe in most metallic systems’. In order to explain an enhanced value of the EFG at  $\text{Hf}_2$  positions, the same group of authors proposed some other mechanism that should be responsible for this. That is, they made an analogy between the situation occurring in the compound  $\text{Hf}_2\text{Fe}$ , and that for diluted Cu alloys. The later situation has been theoretically investigated in reference [17]. The authors of this reference (Dederichs *et al*) were considering a copper lattice, doped with 3d and 4sp impurities (titanium to arsenic), and evaluated the EFG at the Cu atoms in the first-neighbour shell around the impurity. They concluded that hybridization between 3d (or 4sp) states of the impurity atom and d states of the neighbouring copper atoms takes place, leading to the formation of bonding and antibonding states. The antibonding states were found to be responsible for the major part of the EFG at copper sites. On the basis of the physical picture described, the authors of reference [4] assumed that hybridization between 5d states of Ta and 3d states of Fe occurred, proposing this mechanism to be responsible for the enhancement of the EFG at  $\text{Hf}_2$  sites in the compound  $\text{Hf}_2\text{Fe}$ . Incorrectly interpreting the results presented in reference [17], they considered the  $\text{Hf}_2$  position in  $\text{Hf}_2\text{Fe}$  to be similar to the impurity position in dilute Cu alloys. Understanding the values for  $V_{ZZ}$  in reference [17] as the EFG values for the impurity position, they expected that ‘... the d–d contribution to the formation of the EFG at  $\text{Hf}_2$  sites dominates over the p–p contribution, since Ta ions belong to the beginning of the 5d transition series’. Since the EFG at the impurity position in dilute Cu alloys is equal to zero, because this position is surrounded by the atoms of the same species (Cu atoms) and has a cubic symmetry, it is clear that the impurity position should be related to the Fe position, while the Cu sites should be related to the  $\text{Hf}_2$  sites in  $\text{Hf}_2\text{Fe}$ . On interpreting the results of reference [17] properly, the conclusion concerning the different contributions to the EFG remains almost the same. If the hybridization mechanism described above is responsible for the major part of the EFG at  $\text{Hf}_2$  sites in  $\text{Hf}_2\text{Fe}$ , then the d–d contribution should be larger than the p–p contribution (but not as dominant as it is stressed to be in reference [4]), since Fe (not Ta) atoms belong to the middle of the 3d transition series. This conclusion directly follows from the theoretical results of Dederichs *et al* [17].

Our calculations did not support the above-described assumptions about the origins of the EFGs at inequivalent Hf positions in the  $\text{Hf}_2\text{Fe}$  lattice.

At  $\text{Hf}_2$  sites, the EFG practically consists of the contribution from the p electrons only (table 2). This fact implies that the hybridization mechanism investigated in reference [17] is not applicable to the case of  $\text{Hf}_2$  sites in the compound  $\text{Hf}_2\text{Fe}$ . According to PDOS pictures (figure 2) of the electronic structure, hybridization between Fe d and  $\text{Hf}_2$  d states, as well as between Fe d and  $\text{Hf}_2$  p states, certainly exists. However, this mechanism probably does not play an important role in the formation of the EFG. Since the situation in which the contribution from p electrons dominates the EFG is common for most of the HCP metals [8, 14, 18, 19], the

explanation of the origin of the EFG at  $\text{Hf}_2$  sites in  $\text{Hf}_2\text{Fe}$  is likely to be the same as that for the well known test case [14]. That is, because of the factor  $1/r$  which enters the radial integrals used for an evaluation of the components of the EFG tensor (see formulae in reference [9]), the region closest to the nucleus is the most important in determining the magnitude of the EFG. In this region, the 6p wave function of Hf has its first node at distances much closer to the nucleus than that of the Hf 5d wave function, and consequently dominates the EFG. Thus, for the EFG at  $\text{Hf}_2$  positions, it can be said that it is induced in 'the usual way'. An additional argument in favour of this statement is provided by the fact that the EFG at Hf atoms in their elementary hexagonal close-packed (HCP) lattice is dominated by p electrons also. That is, we performed the FP-LMTO ASA calculations for the pure HCP Hf and obtained:  $V_{ZZ} = +9.7$ , the p-p contribution being +7.4, the d-d contribution +2.8, and the f-f contribution  $-0.3$  (in units of  $10^{17} \text{ V cm}^{-2}$ ). This result is in accordance with previously evaluated EFG values for HCP Hf [19]. Analysing the  $\text{Hf}_2$  position and its immediate surrounding (which were nicely presented in figure 2 and table 3 in reference [10]), it can be seen that the  $\text{Hf}_2$  atom has 14 neighbours in the first coordination polyhedron. Of this number, only four neighbours are Fe atoms, while the remainder consists of the Hf atoms. This is another indication that the situation at  $\text{Hf}_2$  sites in  $\text{Hf}_2\text{Fe}$  can be related in some way to the situation occurring for pure HCP Hf.

The results for the EFG at  $\text{Hf}_1$  positions seem to be more intriguing than the ones for that at  $\text{Hf}_2$  positions. The contribution to the EFG from 5d electrons is larger than the contribution from 6p electrons of Hf at these sites (table 2). A suppression of the contribution from p electrons causes a significantly smaller (per modulus) magnitude of the EFG at  $\text{Hf}_1$  sites, compared to the magnitude of the EFG at  $\text{Hf}_2$  sites. The different magnitude of the EFG and the reversed ratio of the contributions from p and d electrons indicate the existence of a different mechanism of formation of the EFG at  $\text{Hf}_1$  sites compared to the EFG at  $\text{Hf}_2$  sites. The  $\text{Hf}_1$  site in the compound  $\text{Hf}_2\text{Fe}$  has twelve neighbours in the first coordination polyhedron: six Fe atoms and six  $\text{Hf}_2$  atoms [10]. The Fe atoms are situated at smaller distances from the  $\text{Hf}_1$  position than the  $\text{Hf}_2$  atoms (2.627 Å versus 3.074 Å respectively). This makes the probability of the formation of the hybrid states between 5d states of  $\text{Hf}_1$  and 3d states of Fe much larger than in the case of the  $\text{Hf}_2$  site. This fact, together with the relation between the magnitudes of the p-p and d-d contributions, indicates that a hybridization mechanism similar to the one in reference [17] could be responsible for the formation of the EFG at  $\text{Hf}_1$  sites in  $\text{Hf}_2\text{Fe}$ . The only qualitative distinction between the EFGs evaluated at Cu sites in the vicinity of the Fe impurity and  $\text{Hf}_1$  sites in the compound  $\text{Hf}_2\text{Fe}$  is in the sign of the p-p contributions (plus in the first case and minus in our case). This distinction may be caused by the different symmetries of the sites. While at Cu sites in dilute Cu alloys the principal component of the EFG is pointed toward an impurity atom [17], this is not the case at  $\text{Hf}_1$  sites in  $\text{Hf}_2\text{Fe}$ .

Finally, the experimentally established facts concerning the temperature dependencies of the EFGs at Hf sites in  $\text{Hf}_2\text{Fe}$  are not in conflict with our suggestion concerning the origin of the EFGs at these sites. At the  $\text{Hf}_1$  position, the magnitude of the EFG exhibits a great sensitivity to the temperature changes. Since raising the temperature corresponds to the rearrangement of the positions of the  $\text{Hf}_1$  neighbours, this sensitivity indicates that in the formation of the EFG some mechanism which includes significant participation of the neighbouring atoms should be involved. That is exactly the case with the hybridization mechanism which we proposed to be responsible of the formation of the EFG at  $\text{Hf}_1$  sites. On the other hand, the magnitude of the EFG at the  $\text{Hf}_2$  site is much less influenced by the changes of the temperature. This is also in accordance with our proposal concerning the origin of the EFG at this position, because changes of the distances of neighbours cannot affect much the region closest to the nucleus, where the first node of the 6p wave function is situated.

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