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Cluster approach to the Ti_2Ni structure type

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It has been established that the 16(*c*) first coordination clusters in the Ti_2Ni structure type (space group $Fd3m$) follow icosahedral-face orientational ordering along regular tetrahedron edge directions. The actual crystal structure appears due to the prevalence of the face-centred cubic translational ordering over the cluster assembling. This way, the competition of the 'regular' crystal phase and its icosahedral analogue is reconstructed at the atomic level. The model accounts for the markedly different electronic characteristics at the different crystallographic positions obtained by hyperfine interaction measurements, and other curious experimental facts help to create an exact physical definition of the first coordination in the solid state and to distinguish between various structure types on fundamental principles.

1. Introduction

The electronic principles of the formation, ordering and stability of various metallic phases is an issue to which extensive experimental and theoretical work has been devoted. Such an approach provides insight into the interactions at the atomic scale level, allowing material properties to be understood and influenced in the most efficient way. Among the most powerful methods for the investigation of the local electronic properties in the solid state are various techniques of hyperfine interaction (HFI) measurements (Heer & Novey, 1959; Kaufmann & Vianden, 1979). Extensive investigations of the Hf_2TM (TM-transition metal) intermetallic compounds (Vulliet *et al.*, 1984; Cekić *et al.*, 1988; Akselrod *et al.*, 1990; Koički *et al.*, 1993; Ivanović *et al.*, 1999; Forker *et al.*, 1999), of the Ti_2Ni structure type using the time-differential perturbed angular correlation of γ-rays (TDPAC) technique, have shown that the intensities of the principle component V_{zz} of the electric field gradient (EFG) at 16(*c*) and 48(*f*) crystallographic positions differ by almost an order of magnitude (Fig. 1). A metallic system with a cubic symmetry should exhibit a low, theoretically vanishing EFG (Heer & Novey, 1959), so the observed results suggest that the 'metallic' nature of the charge distribution, and the symmetry influencing EFG, are violated in these compounds in different ways at the two crystallographic positions [48(*f*)] and [16(*c*)]. This large disparity is evidence of the curious fact that the same type of atom (Hf) obeys different bonding mechanisms at the two positions separated by only ~ 3 Å in the single, well defined crystal structure. Why and how it happens remained unexplained. The other EFG parameters and their temperature dependencies at the two positions also differ significantly, as well as some of the parameters at equivalent positions between various isostructural compounds. These results emphasized that familiar concepts (Kaufmann & Vianden,

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1979; Das & Schmidt, 1985), which relate EFG and electronic structure, are inappropriate for these intermetallic systems. Although further experiments (Soubeyroux *et al.*, 1987; Teisseron *et al.*, 1987; Kuentzler & Waterstrat, 1988; Cekić *et al.*, 1991, 1993; Ivanović, 1997; Ivanović *et al.*, 1995; Cekić *et al.*, 1998) and calculations (Lalić, Popović & Vukajlović, 1998; Lalić, Cekić, Popović & Vukajlović, 1998; Lalić *et al.*, 1999; Cekić *et al.*, 2004) have provided new valuable results, a model capable of accounting for the numerous strange, and at first sight contradictory, observations was lacking. The fact that the electronic distribution at the particular crystallographic position is so exclusive and strictly locally determined motivated the search for structural manifestations of these electronic features. All experimental and numerical results about the investigated compounds available to the authors have been reconsidered and many additional calculations and derivation based mainly on the existing experimental data have been performed. The result is the presented cluster model of the Ti_2Ni structure type. Besides the answers to the questions mentioned above, it provides valuable criteria for the definition of a cluster in a complicated metallic system, pointing out its differences from other structural motives. From these considerations, an exact and general definition of the first coordination in the solid state, and a demarcation of structures on fundamental principles governing their ordering, naturally emerge.

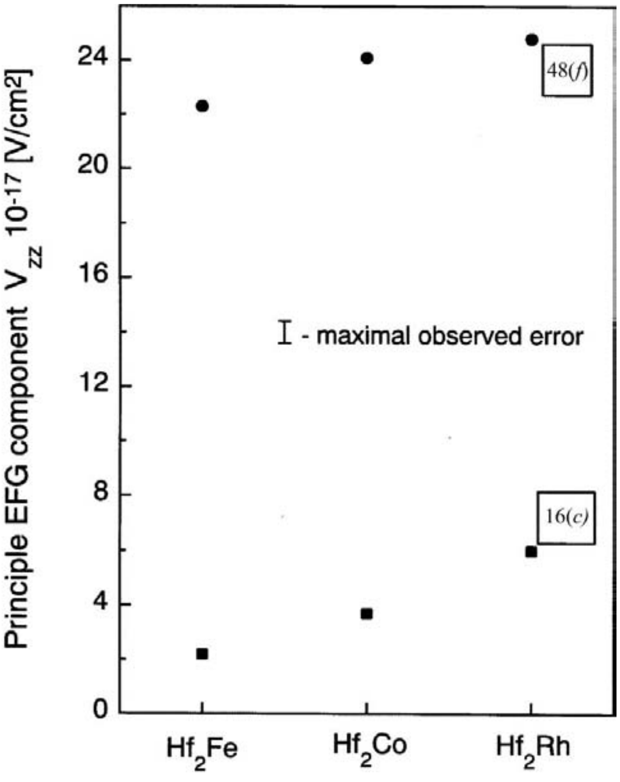

Figure 1
Room-temperature EFG values (V_{zz}) obtained by the time-differential perturbed angular correlations of γ-rays.

2. Results

The results presenting the model in the most transparent manner are as follows. The principal components, V_{zz}, of the EFG at 16(*c*) and 48(*f*) crystallographic positions for three Hf intermetallic compounds of the Ti_2Ni structure type at room temperature are presented in Fig. 1.[1] Low values at the 16(*c*) position imply homogeneous, 'metallic' charge distribution, while the large EFG values at 48(*f*) indicate the existence of a highly localized, directional charge distribution of the 'covalent' type.

The structure of the first coordination clusters at 16(*c*), 32(*e*) and 48(*f*) crystallographic positions is presented in Fig. 2 and Table 1.[2] Interatomic distances at the 16(*c*) position are very short and grouped in the two distinct groups (six Hf—TM and six Hf—Hf), according to the size of the atoms involved and the peculiarities of their interactions. All the distances inside each group are equal, implying that the corresponding bonds are equivalent. Conversely, at the 48(*f*) positions there are five different interatomic distances, which vary considerably even for the bonds between the same type of atoms (for instance, three different Hf—Hf distances). A markedly pronounced gap between the first and the second coordination exists at all the positions. Bond-length deviations from 'ideal' icosahedral values are also given in Table 1 for the 16(*c*) (marked by *) and the 32(*e*) (marked by **) clusters. The 'ideal' icosahedral bond lengths are obtained by minimizing the deviation of all the distances of the real from the ideal icosahedral values.

The results of tight binding (TB) calculations of the first coordination clusters, performed according to the formalism and parameterization developed in Pettifor (1996) and Harrison (1999), are presented in Fig. 3. The hopping integrals are evaluated according to the formulae (Harrison, 1999)

$$V_{l'lm} = \eta_{l'lm} \frac{\hbar^2 (r_{l'}^{2l'-1} r_l^{2l'-1})^{1/2}}{m_e R^{l'+l+1}}$$

$$\eta_{l'lm} = \frac{(-1)^{l+m+1}(l+l')!(2l)!(2l')!}{6\pi 2^{l+l'} l! l'!} \times \left[\frac{(2l+1)(2l'+1)}{(l+m)!(l-m)!(l'+m)!(l'-m)!}\right]^{1/2}$$

where $l, l' = s, p, d$ are orbital moments of the atomic states, $m = 0, 1, 2$ is the angular momentum, $\hbar$ is the reduced Planck's constant, m_e is the electron mass, r_l is the l state radius and R is the interatomic distance.

The principle idea was to consider the stabilities of the first coordination clusters as being separate entities, as which they might appear in the melt during the initial stages of the nucleation process, for instance. The connection to actual structures is made by choosing the experimental distances from Table 1 as the equilibrium distances for the Ti_2Ni-type structures, and those of ideal icosahedra, for the corre-

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[1] Fig. 1 is compiled from the experimental data presented in Koički *et al.* (1993), Ivanović *et al.* (1999) and Cekić *et al.* (2004).

[2] These results are derived from experimental data presented in Cekić *et al.* (1991, 1993), Ivanović (1997), Ivanović *et al.* (1995) and Cekić *et al.* (1998).

Table 1
Bond lengths, bond shortening (▸) and bond deviations from the values of the ideal 16(*c*) (*) and 32(*e*) (**) icosahedra, in the first coordinations of Hf_2TM (TM = Fe, Co, Rh) intermetallic compounds.

Bond shortening is taken to be the difference between the sum of the atomic radii for the metallic coordination 12 (Wells, 1975) and the corresponding measured distance.

			Distance (Å)		
			(▸) Bond shortening (Å)		
			(*), (**) Icosahedral deviation (Å)		
Position	Bond	Number of bonds	Hf_2Fe	Hf_2Co	Hf_2Rh
16(*c*)	Hf1—*X*	6	2.627 (5)	2.656 (9)	2.784 (9)
			▸0.223	0.184	0.182
			(*) 0.3350	0.3230	0.2910
	Hf1—Hf2	6	3.074 (2)	3.081 (3)	3.158 (5)
			(▸) 0.106	0.099	0.022
			(*) −0.1120	−0.1000	−0.0830
32(*e*)	*X*—Hf1	3	2.627 (5)	2.656 (9)	2.748 (9)
			(▸) 0.223	0.184	0.182
			(**) 0.3350	0.3310	0.3330
	X—Hf2	3	2.80 (1)	2.77 (2)	2.758 (9)
			(▸) 0.050	0.070	0.172
			(**) 0.1620	0.2170	0.3230
	X—*X*	3	2.94 (1)	3.044 (4)	3.26 (1)
			(▸) −0.280	−0.270	−0.078
			(**) 0.0220	−0.0570	−0.1790
	X—Hf2	3	3.061 (3)	3.06 (3)	3.13 (1)
			(▸) −0.211	−0.220	−0.200
			(**) −0.0990	−0.0730	−0.0490
48(*f*)	Hf2—*X*	2	2.80 (1)	2.77 (2)	2.758 (9)
			(▸) 0.050	0.070	0.172
	Hf2—*X*	2	3.061 (3)	3.060 (4)	3.13 (1)
			(▸) −0.211	−0.220	−0.200
	Hf2—Hf1	2	3.074 (2)	3.081 (3)	3.158 (5)
			(▸) 0.106	0.099	0.022
	Hf2—Hf2	4	3.173 (2)	3.198 (2)	3.303 (7)
			(▸) 0.007	−0.018	−0.123
			(*) −0.2110	−0.2170	−0.228
	Hf2—Hf2	4	3.236 (5)	3.256 (5)	3.258 (2)
			(▸) −0.056	−0.076	−0.077
			(**) −0.2740	−0.2690	−0.1770

sponding icosahedral phases. Then some parameters of the hopping integrals were adjusted to reproduce the *d*-band widths, as obtained by the *ab initio* calculations (Lalić *et al.*, 1999; Cekić *et al.*, 2004). Although the method is very simple, in the first approximation it accounts for the effects of *s*–*d* hybridization, local charge neutrality and diagonal disorder. It does not provide absolute accuracy better than 1 eV, but it does provide fundamentally correct trends (Pettifor, 1996; Harrison, 1999) so the fact that it is applied to similar structures from similar atoms in a consistent manner gives hope that the trends presented in Fig. 3 are reliable. The results obtained imply that the 16(*c*) first-coordination cluster is the most stable unit of the structure in all the compounds, and that the real clusters are more, or at least equally (Hf_2Co case), stable than the corresponding ideal ones.

In Fig. 4 the arrangement of the 16(*c*) first-coordination clusters in the Ti_2Ni unit cell is presented. The central atoms occupy positions at the regular tetrahedral edges along [100], [010], [001], [$\bar{1}$01], [1$\bar{1}$0], [0$\bar{1}$1] f.c.c. (face-centred cubic) primitive directions of the vectors. The clusters always join by the same triangle from the two TM and one Hf(2) ions, which is marked in Fig. 2 for the [100] direction. To preserve the same relative position of the joining triangle in two successive clusters, every second cluster in the chain rotates 180° around the tetrahedral edges (icosahedral face axes). This regular and continual arrangement, known as icosahedral face-orientational ordering, adopted along the directions mentioned, forms the Ti_2Ni-type crystal structure.

The central atoms of the 32(*e*) first coordinations form compact TM tetrahedra (Fig. 2), with each TM tetrahedron being embedded between the two 16(*c*) coordinations in a regular way (Fig. 4). The centres of these tetrahedra, which are found to be responsible for the interesting magnetic behaviour of the Hf_2Fe compound upon hydrogenation (Buschow & VanDeepen, 1979; Vulliet *et al.*, 1984; Soubeyroux *et al.*, 1987; Teisseron *et al.*, 1987; Forker *et al.*, 1999), mimic diamond positions inside the Ti_2Ni unit cell (Yang, 1988). Using the *HyperChem* software package (Hypercube, Inc., 1994) we performed *ab initio* LCAO (linear combination of atomic orbitals) calculations of the neutral and one-electron (positively and negatively) charged Fe and Co tetrahedra with dimensions as experimentally established in the Laves phases [$HfFe_2$, Fe—Fe distance is 2.484 Å (Ivanović *et al.*, 2000), $HfCo_2$, Co—Co distance is 2.443 Å (Ivanović *et al.*, 2000)], Ti_2Ni structure-type compounds [Hf_2Fe, Fe-Fe distance is 2.94 Å (Cekić *et al.*, 1991), Hf_2Co, (Co—Co distance is 3.044 Å (Cekić *et al.*, 1993, 1998)] and the intermediate distance (d = 2.7 Å) between these two. Regardless of the charge state and dimensions, an isolated Fe—Fe tetrahedron is only stable in the magnetic triplet state. The moments are unevenly distributed among the atoms and frustrated, with an average moment of ~ 1.7 μ_B per Fe atom, for the Hf_2Fe neutral tetrahedron. The experimentally determined values in hydrogenated compounds are 0.9 μ_B (Buschow & VanDeepen, 1979) and 1.5 μ_B (Soubeyroux *et al.*, 1987) per Fe atom, with the Fe—Fe distance estimated to be 2.84 Å. The calculations indicate that similar Co tetrahedra are much more stable both in the non-magnetic singlet and magnetic triplet states than the Fe analogues.

3. Discussion

3.1. Position 16(*c*)

This coordination cluster is the simplest and the most stable local structure which when arranged in a specific way, reproduces the Ti_2Ni crystal structure type (Fig. 4). Consequently, its local features and the pattern of its arrangement should determine the principal material properties.

The considerable amount of electron transfer between *s*, *p* and *d* shells observed by the calculations (Lalić *et al.*, 1999; Cekić *et al.*, 2004), and collectivization of valence electrons due to the resonant metallic bonding, expressed in the low V_{zz} values observed at this position (Fig. 1), are reasons for the prominent structure contraction which is similar to that which has been seen in some icosahedral crystals (Janot, 1997). The phenomenon can be explained as an attempt by the structure to reach one of the 'magic numbers' of the cluster valence-electrons of exceptional stability and to maximally saturate the resonant bonds at the same time.

The high symmetry of the 16(c) first coordination and the tendency of the Hf1 ion at the position to surround itself by as many X ions as possible (twice as many as the formula unit) also suggest its ‘metallic’ nature. The density-of-states (DOS) features, mainly determined by the d-state attributes (Lalić *et al.*, 1999; Cekić *et al.*, 2004; see Fig. 5) also support that. The Fermi level values are rather high and a typical DOS shape characterizes the structures that provide each d wavefunction to simultaneously build a large number of bonds (Fridel, 1969). Although the number of TM atoms in the first coordination of the 16(c) position (6) is higher than at the 48(f) position (4), the TM-d states peak below E_f is slightly lower at 16(c) than at 48(f) (Lalić *et al.*, 1999; Fig. 1), see Fig. 5(a). Furthermore, the huge peak of the Hf d states just above the Fermi level, visible at 48(f) is almost completely absent at the 16(c) position, see Figs. 5(a) and (b) (Lalić *et al.*, 1999; Fig. 1). Both features are consequences of a strong s,p–d hybridization existing at the 16(c) position.

While the electronic states of identical clusters must be exactly alike (Bader, 1995; Janot, 1997), the observed rotation of the 16(c) icosahedra (Fig. 4) is not only an extension of the icosahedral symmetry along particular directions (Shoemaker & Shoemaker, 1988), but also a local structural manifestation of the continuity condition of the electronic states, ensuring their identity at the cluster border. Inside the 16(c) corridors the electron ‘sees’ the same environment at both sides of the joining triangle. Along these directions the long-range coherence of the cluster wavefunction is preserved, which must strongly influence the transport characteristics of the materials (Yakhot *et al.*, 1990; Wang *et al.*, 1993; Roitsin *et al.*, 1997). The long-range ordering of 16(c) endohedral icosahedra could be connected with the superconductivity observed in some of these compounds (Kuentzler & Waterstrat, 1988).

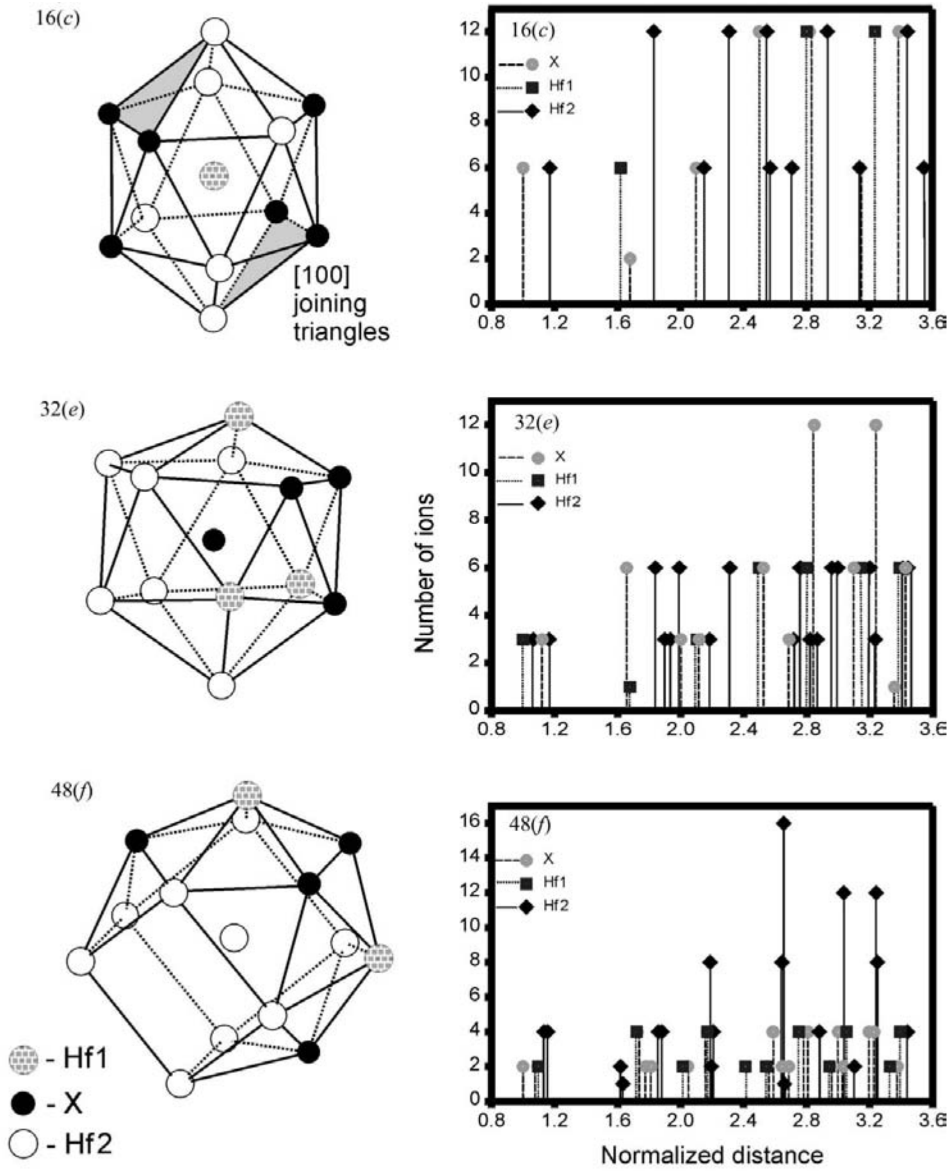

Figure 2
The structure of the 16(c), 32(e) and 48(f) first coordination clusters of the Ti_2Ni structure type.

The electronic constitution of the 16(c) cluster should also explain the curious temperature behaviour of the EFG parameters (Koički *et al.*, 1993; Ivanović, 1997; Ivanović *et al.*, 1999; Cekić *et al.*, 2004) and the specific heat C_p (Kuentzler & Waterstrat, 1988; Ivanović *et al.*, 1995), indicating the existence of a phase transition in the compounds. The fact that an endohedral ion in the icosahedral environment can attain several non-central positions with energies very close to the ground state (Roitsin *et al.*, 1997) allows its displacement bellow the critical temperature T_c, where the competition between the translational and bond-orientational ordering is strong. Above T_c, a redistribution of the electronic states of the displaced central ions leads to the ‘regular’ linearly descending $V_{zz}(T)$ behaviour (Akselrod *et al.*, 1990; Koički *et al.*, 1993; Ivanović, 1997; Cekić *et al.*, 2004) and to the ordering of ions at the regular lattice positions, relaxing the local structure internal strain, as indicated by the shape of the $C_p(T)$ curves (Ivanović *et al.*, 1995). The fact that the central ions below T_c occupy energetically almost equivalent but spatially slightly different positions also explains why the EFG distribution parameter δ is an order of magnitude higher at the 16(*c*) position than at the 48(*f*) position in all the Hf_2TM compounds measured (Akselrod *et al.*, 1990; Koički *et al.*, 1993; Ivanović, 1997; Ivanović *et al.*, 1999; Cekić *et al.*, 2004). Above T_c, δ at 16(*c*) approaches the expected values. The critical temperatures observed (430, 560, 620 K, for Hf_2Fe, Hf_2Co and Hf_2Rh, respectively; Koički *et al.*, 1993; Ivanović *et al.*, 1995, 1999; Ivanović, 1997) are in the range of the critical temperatures of the quasicrystals found in other similar intermetallic compounds, for instance, $T_c \simeq 670$ K in $(Ti_{1-x}V_x)_2Ni$ (Zhang *et al.*, 1985).

Values of the asymmetry parameter η, which reflect the symmetry of the position, actually deviate from the theoretically predicted value of $\eta = 0$ in all the compounds (Ivanović, 1997; Ivanović *et al.*, 1999; Cekić *et al.*, 2004). The deviation is the smallest for Hf_2Fe, but in the compounds that are more difficult to synthesize, *e.g.* those with poorly formed Ti_2Ni structure, Hf_2Rh (Ivanović *et al.*, 1999) and Hf_2Co (Ivanović, 1997; Cekić *et al.*, 2004) the deviation from $\eta = 0$ is sizeable. As a consequence, in order to reproduce fairly their experimental data, whilst obeying the constraint $\eta_{16c} = 0$, some authors (Akselrod *et al.*, 1990; Van Eek & Pasquewitch, 1999) had to introduce two high-frequency interactions. The deviation of the asymmetry parameter η from its theoretical value is more proof that the charge distribution in these complicated systems is influenced mainly by the first coordination cluster properties, the higher the T_c value, and that poorly follows the Ti_2Ni unit-cell symmetry requirements. The measurements (Ivanović *et al.*, 2000; Belošević-Čavor *et al.*, 2004) have shown that this is not the case for the Laves phases of these elements and that their EFG parameters are well suited to the unit-cell characteristics, even in the samples in which the structure is incompletely formed, or in which a strong competition between phases (C15 and C14) exists.

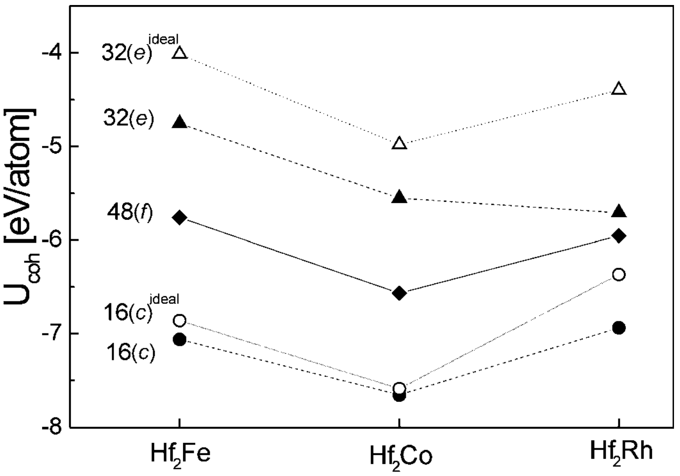

Figure 3
Cohesive energy of the 16(*c*), 32(*e*) and 48(*f*) first-coordination clusters obtained by tight-binding calculations. The values of the ideal icosahedra are presented by empty symbols.

3.2. Position 32(*e*)

The icosahedral structure of the 32(*e*) first coordination (Fig. 2), its presence both in the Ti_2Ni and the quasicrystalline phase (Yang, 1988), good stoichiometry and low EFG (Lalić *et al.*, 1999), explicate it to be a natural complement to the fundamental building block [16(*c*) first coordination]. The rather uniform spatial charge distribution (low EFG) that exists despite a highly asymmetric grouping of the like and unlike first-nearest neighbours in this coordination (Fig. 2) can be explained by the primacy of the *s*,*p*–*d* interaction, which recognizes only the principle topology of the first coordination cluster, over the direct *d*–*d* overlap, which distinguishes the neighbouring atoms.

The LCAO calculations show that some magnetic characteristics of Hf–TM compounds can be related to the intrinsic properties of the TM-ion tetrahedra, which, in different spatial arrangements, exist both in the 32(*e*) first coordination cluster

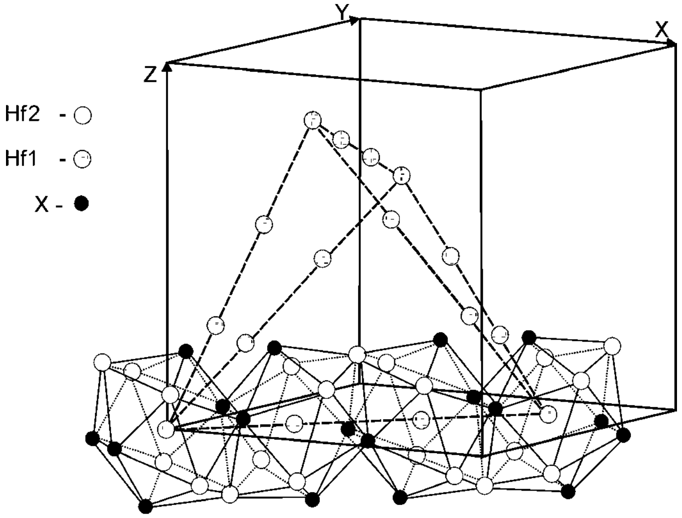

Figure 4
The arrangement of the 16(*c*) coordination clusters in the unit cell. The central atom Hf1 positions, forming a regular tetrahedron in the unit cell, are connected to guide the eye. The manner in which the clusters join each other is given for the [100] direction of the f.c.c. primitive vectors.

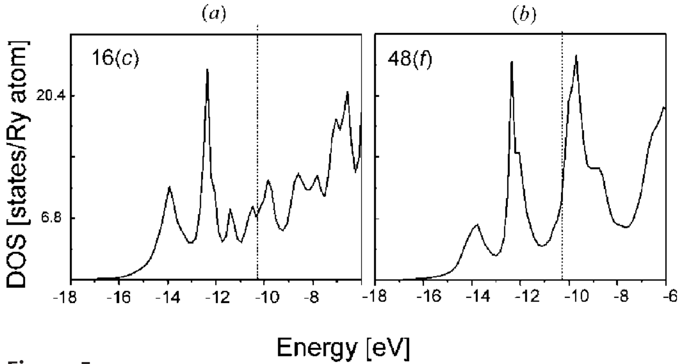

Figure 5
Density-of-states calculated for the appropriate clusters of 168 atoms around (*a*) 16(*c*) and (*b*) 48(*f*) crystallographic positions of the Hf_2Co compound, using the *FEFF*8.2 program package (Ankudinov *et al.*, 1998). Fermi level is denoted by dotted lines.

of the Ti_2Ni structure type and Laves phases. Although the Fe tetrahedron is inherently magnetic in its stable triplet state, this state and macroscopic manifestation of magnetism in Hf_2Fe is suppressed by the strong Hf—Fe *s*, *p*–*d*-band interaction, which delocalizes Fe *d* electrons. It was experimentally observed (Buschow & VanDeepen, 1979; Soubeyroux *et al.*, 1987; Teisseron *et al.*, 1987) that on hydrogenation of Hf_2Fe, the Fe tetrahedra contract while the rest of the structure expand, and the macroscopic magnetic moment appears. The reason for this is a strong *s*–*s* Hf—H interaction (Papaconstantopulos & Switendick, 1984) which is present in the hydrogenated compound, which releases the Fe *d* electrons from the bonds they are involved in. These electrons then become more localized and the intrinsic magnetic properties of the Fe tetrahedra become evident. The fact that the Hf—H interaction influences the magnetic moment on Fe in such a resolute manner is further proof that in the pure Hf_2Fe compound Hf *s* electrons strongly interact with Fe *d* electrons. A similar tetrahedron of Co atoms in Hf_2Co is exceptionally stable both in the non-magnetic singlet and the magnetic triplet states. Owing to the band effects (Cekić *et al.*, 2004), which favour the non-magnetic state in the ordered compound, the appearance of magnetism upon hydrogenation in Hf_2Co should not be expected. Likewise, the $HfFe_2$ Laves phase is ferrimagnetic, while $HfCo_2$ is enhanced paramagnetic. This specific type of paramagnetism demonstrates an inherent ability of the Co tetrahedron to achieve the other stable state, the magnetic triplet state, when the specific conditions for that are fulfilled. In both cases, more definite judgement requires more detailed calculations for various tetrahedron interatomic distances and charges, as well as detailed first-principle band structure calculations, which are in progress.

3.3. Position 48(*f*)

The ‘covalent’ type of bonding, manifested in large EFG (Fig. 1) and specific DOS features (Lalić *et al.*, 1999; Fig. 5*b*) compensates for the low symmetry of the first coordination cluster and the small number of TM ions it contains. The largest charge inhomogenities (EFG component V_{zz}) at this position and the whole system (Lalić *et al.*, 1999) are parallel to the tetrahedron edges connecting the 16(*c*) positions, as presented in Fig. 4. As in some A15 structure-type intermetallic compounds with icosahedral structural motives (Kaufmann & Vianden, 1979; Lu & Klein, 1997), EFG and internal strain in the Hf_2TM compounds are related and the largest EFG’s occur for the directions along which the tiling of the 16(*c*) icosahedra is forced to fulfil the conditions for the Ti_2Ni unit-cell formation. Significant variation among the bond lengths of the same type (Table 1) is also a sign of a strained structure.

The coordination does not form a regular substructure or any kind of long-range order. It follows the arrangement of the 16(*c*) and 32(*e*) icosahedra, filling the empty space, which appears during the Ti_2Ni structure formation. From that one can conclude that the 48(*f*) first coordination is just an outcome of the competition between the face-icosahedral orientational and f.c.c. translational ordering formed according to the prevailing phase (Ti_2Ni) stability and symmetry requests. The 48(*f*) first coordination cluster structure appears exclusively in the Ti_2Ni structure type (Villars *et al.*, 1989) and shows how the icosahedral frustration is relieved in this particular case. The appearance of another high-frequency HFI (Vulliet *et al.*, 1984; Akselrod *et al.*, 1990; Van Eek & Pasquewitch, 1999), in the samples in which the Ti_2Ni structure failed to arrange completely is easily understood in this framework. The local structure of the main building blocks [16(*c*) and 32(*e*) first coordination clusters] is not substantially affected, but the details of their arrangement expressed through the 48(*f*) cluster are, and another high-frequency interaction appears.

4. Conclusions

By exploring the sensitive dependence of the EFG parameters on the local electronic environment, an atomic scale insight into the Ti_2Ni structure-type has been obtained. Different types of bonding at distinct local positions of the Hf_2TM compounds established both by HFI measurements and calculations arise from different physical mechanisms of the first-coordination cluster formation and their roles in the unit cell and long-range ordered structures of the compounds. In the initial stage of the primary nucleation, the strong interaction of unlike-atoms favours the formation of an icosahedral cluster [16(*c*) first coordination] with twice as many TM ions than the formula unit provides. This cluster is more stable than the other two and essentially metallic, with homogenous charge distribution, low EFG and short interatomic distances. The formation of the structure proceeds along with the face-icosahedral orientational ordering of the 16(*c*) clusters, following a tetrahedral pattern (Fig. 4). After the fourth cluster is placed along each tetrahedron edge, the f.c.c. translation ordering prevails over the icosahedral ordering, a possibility predicted a long time ago (Jarić, 1985), but, as far as we know, explicitly recognized here for the first time in a ‘classical’ structure type. As a result, the Ti_2Ni unit cell emerges. This is enabled by the fact that the deformed icosahedra, which appear in the Ti_2Ni structure type Hf—TM compounds, are more or at least equally stable than their ideal counterparts (Fig. 3). The 32(*e*) first-coordination cluster also has an icosahedral atomic arrangement, a large number of unlike neighbours, low EFG and appears both in the Ti_2Ni and the relating quasicrystalline phase as a natural complement of the 16(*c*) cluster. The 48(*f*) first coordination could not be classified as a genuine cluster with steady and transferable properties, but only as a by-product of the Ti_2Ni structure-type formation, expressing the way in which the conflict between the tendency towards the local atomic icosahedral arrangement (governed by the atomic interaction) and the tendency of filling the space in a dense manner (governed by the structure ordering) is resolved for this particular structure type. The low number of unlike first neighbours and large variations of the length among the bonds of the same type imply the existence of a considerable local strain at this position and 'covalent' bonding appears to compensate for it.

The presented model of the Ti_2Ni structure type is much simpler than any proposed previously (Yang, 1988; Pauling, 1989) and in some aspects similar to the icosahedral glass (Stephens, 1989) model. It predicts that the structure is formed of simple, inherently stable icosahedral clusters that can exist in liquid as well as in various condensed phases. Multiple remelting and long annealing is necessary to obtain a good quality Ti_2Ni phase, which is a usual feature of the structures whose building units share common faces or volume. The remarkable dependence of the surface roughness of the samples on annealing (Cekić *et al.*, 1998), with the bond lengths remaining practically unaffected (Cekić *et al.*, 1998; Ivanović *et al.*, 1999), and the already mentioned dependence of the C_p and EFG parameters on temperature, also support an entropy-governed model of the formation of the Hf_2TM compounds. Therefore, it appears that the behaviour of the EFG parameters can help to distinguish between the entropy-governed or composed structures, in which they are strictly locally adapted and do not 'see' the complete unit cell, and the 'coherent' structures, where they perceive the main features of the entire unit cell.

The model also explains many of the experimental and numerical findings which have been insufficiently elaborated upon in previous papers. The reason for the large difference in the EFG parameters at the 16(*c*) and 48(*f*) positions, the deviation of the 16(*c*) asymmetry parameter from the theoretically predicted value, the dilemma about two high-frequency interactions at the 48(*f*) position, and the nature of the phase transition and its particular connection with the 16(*c*) position seem to be dealt with well by the model.

A logical further step is to relate attributes of these local structures and their arrangement with the macroscopic characteristics of the materials. On that line we discussed the behaviour upon hydrogenation, the influence of the TM tetrahedra on the magnetic characteristics of these materials and their related Laves phases, the exotic specific heat temperature dependence and the existence of superconductivity in some of the compounds. Possible extensions of the cluster approach are numerous. Understanding the fundamental properties of the structural building blocks and the mechanism for their ordering offers the possibility of investigating the nano-sized clusters in their natural environment and to find the general microscopic rules governing the existence, formation and properties of, at the first glance, very different (crystalline, quasicrystalline, amorphous, glass) intermetallics phases. The design of unique materials, such as monolithic intermetallic composites without grain boundaries, is among the possibilities offered by this approach. The behaviour of some intermetallics addressed as 'something between' metals and ceramics can be related to the phases with a regular metallic matrix [16(*c*) coordination three-dimensional network in the Ti_2Ni structure type] 'filled' by the local structures with highly directional charge distribution [48(*f*) coordinations].

Some other interesting ramifications also appear from the model presented. It is established that in the investigated compounds, EFG depends essentially on the charge-distribution topology of the first coordination and the recent calculations (Blaha *et al.*, 1988; Ehman & Fahnle, 1997; Petrilli *et al.*, 1998; Lalić, Popović & Vukajlović, 1998; Lalić, Cekić, Popović & Vukajlović, 1998; Lalić *et al.*, 1999; Cekić *et al.*, 2004) show that this is the case for many other metallic systems. Conventionally the experimental EFG data are presented as the eigenvalues of the electrostatic potential Hessian matrix at the probe-ion position. Since the gradient fields of the electrostatic potential and the charge distribution are homeomorphic (Tal *et al.*, 1980), it is clear, although analytically not straightforward, that the experimental EFG values can be related to chemical bonding by using an appropriate topology theory (Silvi & Savin, 1994; Bader, 1995; Aray *et al.*, 1996; Simak *et al.*, 1997). This directly leads to the exact (and presently lacking) definition of the first coordination in the solid state. Like the molecular structure (Bader, 1995), it should be defined as the minimal atomic arrangement around the particular position of the crystal lattice, which determines the generic properties of its charge distribution topology [number and type of charge-distribution gradient-field (CDGF) critical points]. Any system of atoms has distinct CDGF topological features which exactly reflect its properties, *e.g.* the number and types of atoms, their spatial arrangement and interactions. Consequently, every crystallographic position in the solid state has its unique CDGF topology, which is determined by the number, type, positions and mutual interactions of an exact number of surrounding atoms. These and only these atoms belong to the first coordination cluster. Taking into consideration just one atom less will change the topological features mentioned (number and/or type of CDGF critical points). Taking into consideration one atom more leaves these features unchanged, indicating that this additional atom does not belong to the first coordination cluster. The definition also settles an equivalence class of the structure, making the explicit demarcation between a structural deformation (CDFG topology persists) and a transition (CDGF topology changes) possible. This builds the foundations for some interesting but intuitive topologic approaches to structure classification (Villars *et al.*, 1989).

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