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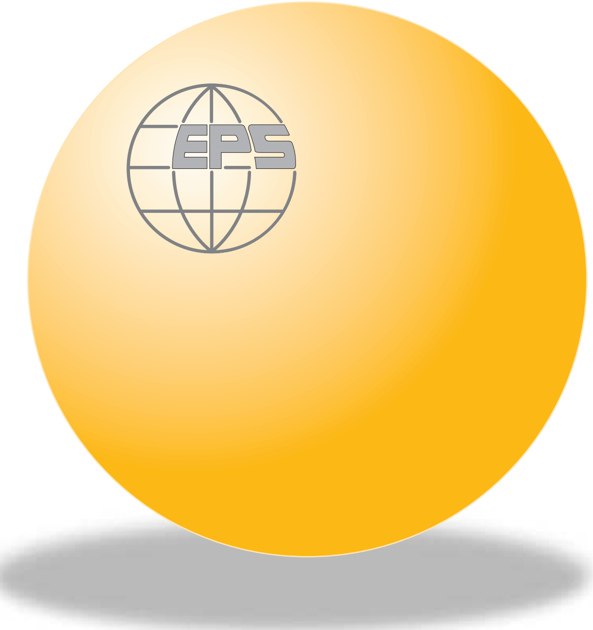

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Phase transition mechanisms in lanthanide elemental crystals

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Abstract. – A unifying theoretical description is given of the phase transition mechanisms occurring in lanthanide elemental crystals. The hcp-9R-dhcp-fcc sequence of reconstructive phase transitions is interpreted in terms of crossover between displacive and reordering mechanisms. The distorted fcc, monoclinic, α-U-type and bct high-pressure phases can be depicted by purely displacive mechanisms, the low symmetry of these phases resulting from the non-spherical shape of the electronic shells induced by the delocalization of the f-electrons.

Two types of atomistic mechanisms are usually invoked for characterizing the physical nature of the order parameters at structural phase transitions. For displacive structural transitions the order-parameter represents a collective displacement of the atoms with respect to the average positions occupied, at equilibrium, in the more symmetric "parent" structure. For order-disorder transitions, the order-parameter consists of the difference between the probabilities assigned to each site in the disordered and ordered phases. For structural transitions of the reconstructive type [1], which are typified by the property that the group-subgroup relationship between the symmetries of the phases surrounding the transition is lost, the two mechanisms —displacive and ordering— often appear as correlated. The collective displacements of the atoms generally induce a reordering of the structure and vice versa. This close connection between displacive and ordering processes stems from the fact that reconstructive transitions realize an intermediate situation between the two mechanisms: on the one hand, the atoms are shifted from their initial to their final positions, without any intermediate position, but the atomic shifts occur collectively; on the other hand, the uncorrelated character of the atomic diffusion is only partly verified. A good illustration of this mixed behavior can be found in the group of elements forming the lanthanide family, in the pressure-temperature phase diagrams of which [2] typical sequences of reconstructive transformations have been found, which can be interpreted alternatively by purely displacive mechanisms or by reordering processes between close-packed structures. The aim of this letter is to give a unifying description of the preceding transformations showing that they can be related to a small number of basic structural mechanisms.

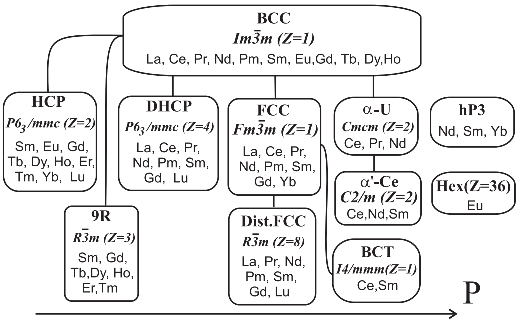

Fig. 1

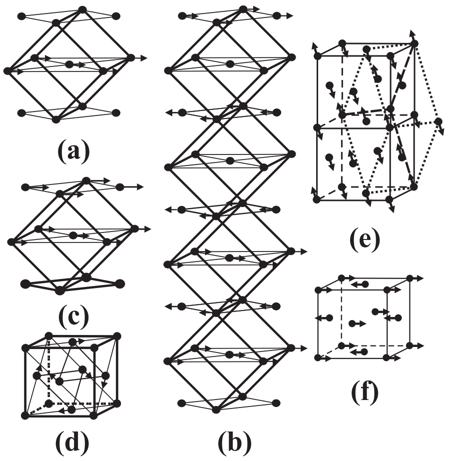

Fig. 2

Fig. 1 – Distribution of the lanthanide elements among their different structures.

Fig. 2 – Atomic displacements associated with (a) Burgers mechanism, (b) the bcc-9R transition, (c) the Bain deformation, (d) the fcc-rhombohedral (distorted fcc) transition, (e) the bcc-monoclinic α'-Ce and (f) bcc-α-U transformation.

Figure 1 shows the structures disclosed for the members of the lanthanide family and the distribution of structures among lanthanide crystals. Let us first show that one can *a priori* give a unifying description of all the lanthanide structures in terms of purely displacive mechanisms occurring from a bcc parent structure. Such picture is justified by the existence of a bcc phase below the melt in the phase diagrams of at least eleven lanthanide elements [3], many of which exhibit a region of coexistence of the bcc structure with the hcp, 9R, dhcp and fcc phases. The displacive transformation mechanisms from the bcc structure can be shared into two types: 1) variants of the Burgers mechanism [4] which give rise to the hcp, dhcp and 9R structures, and 2) variants of the Bain deformation mechanism [5] which yield the fcc, distorted fcc and body-centered tetragonal (bct) structures, the monoclinic and α-U-type structures providing the link between the two preceding variants.

1) The bcc-hcp Burgers mechanism [4] can be formulated [6] in terms of antiparallel shifting of the atoms lying in the $(110)_{\mathrm{bcc}}$ planes along the $\pm[1\bar{1}0]$ directions. It leads to an orthorhombic structure (space-group $Cmcm$, $Z = 2$) which transforms into the hcp structure for the specific shifts $a\sqrt{2}/12$, where a is the cubic lattice parameter, supplemented by spontaneous deformations consisting in tensile $[\zeta_1 \simeq (e_{xx} + e_{yy} - 2e_{zz})]$ and shear (e_{xy}) strains [6]. An alternative description can be given by considering consecutive $(110)_{\mathrm{bcc}}$ layers, numbered $1, 2, 3, 4, \ldots$. The ABAB… hcp structure results from a parallel displacement of the even layers $(2, 4, 6, \ldots)$ by $a\sqrt{12}/6$ along the $[1\bar{1}0]$ direction, the odd layers $(1, 3, 5, \ldots)$ being unshifted (fig. 2(a)). Analogously, the formation of the four-layered dhcp (ABACA…) structure differs only by the property that the even layers are displaced by the same amount $(a\sqrt{12}/6)$ but in antiparallel directions $\pm[1\bar{1}0]$. The bcc-9R displacive mechanism proposed by Wilson and de Podesta [7] represents a further variant of Burgers mechanism. It can be depicted [8] by antiparallel displacements of equal magnitude $(a\sqrt{12}/6)$ in the $[110]_{\mathrm{bcc}}$ direction, of (110) layers numbered 2, 4, 9, and in the $-[110]_{\mathrm{bcc}}$ direction of layers numbered 3, 5, 7, the 1, 6, 8 layers remaining unshifted (fig. 2(b)). The resulting 9R space-group ($R\bar{3}m$, $Z = 3$) is not a subgroup

TABLE I – *Order parameter symmetries for the displacive mechanisms giving rise to the lanthanide phases from the bcc parent phase.* (a) *Phase denomination;* (b) *critical* $\boldsymbol{k}$*-vector of the bcc BZ;* (c) *order-parameter dimensionality;* (d) *equilibrium relationship between the corresponding order-parameter components (only non-zero (active) components are indicated);* (e) *critical shifts;* (f) *secondary strains involved in the transitions.*

(a)	(b)	(c)	(d)	(e)	(f)
hcp	$\mathrm{N}(\frac{1}{2}\frac{1}{2}0)$	6	η_1	$\xi_c = \frac{a\sqrt{2}}{12}$	ζ_1, e_{xy}
α-U	$\mathrm{N}(\frac{1}{2}\frac{1}{2}0)$	6	η_1	–	–
dist.fcc	$\mathrm{N}(\frac{1}{2}\frac{1}{2}0)$	6	$\eta_3 = \eta_6; \eta_4 = -\eta_5$	–	ζ_1
α'-Ce	$\mathrm{N}(\frac{1}{2}\frac{1}{2}0)$	6	η_6	–	ζ_1
dhcp	$\Sigma(\frac{1}{4}\frac{1}{4}0)$	12	$\eta_1 = \eta_2$	$\xi_c = \frac{a\sqrt{2}}{6}$	ζ_1
9R	$\Sigma(\frac{1}{3}\frac{1}{3}0)$	12	$\eta_1 = \eta_2$	$\xi_c = \frac{a\sqrt{2}}{6}$	ζ_1
fcc	$\Gamma(000)$	2	ζ_1	$\xi_c = n\frac{a\sqrt{2}}{6}$	e_1
bct	$\Gamma(000)$	2	ζ_1	–	–

of the bcc space group, since its threefold axis does not coincide with the cubic threefold axes.

2) The bcc-fcc Bain deformation [5] consists in stretching the bcc unit-cell along one of the fourfold axes and compressing it along the other fourfold axes. It can be described in terms of displacements [6, 9]: The atoms belonging to three successive $(011)_{\mathrm{bcc}}$ layers are shifted in the $\pm[110]$ direction by the successive amounts $a\sqrt{2}/6$, $a\sqrt{2}/3$, $a\sqrt{2}/2$, thus forming the ABCA... fcc stacking order (fig. 2(c)). For general displacements in the same directions, the symmetry of the bcc structure is lowered to body-centered tetragonal [9] ($I4/mmm$, $Z = 1$) corresponding to the bct structure found in Ce and Sm [10].

A number of recent studies have confirmed [11, 12] the rhombohedral structure ($R\bar{3}m$, $Z = 8$) of the "distorted fcc" phase found in La, Pr, Nd, Pm, Sm and Gd. In the phase diagram of these elements, this phase is adjacent to the fcc phase to which it is group-subgroup related. The fcc-distorted fcc mechanism is shown in fig. 2(d). It consists of antiparallel displacements of six atoms belonging to the eightfold rhombohedral unit-cell along the face diagonals, *i.e.* in the planes perpendicular to the threefold axes of the initial cubic structure. Two atoms, located at the vertices of the rhombohedral unit-cell, remain unshifted with respect to their fcc positions. The α'-Ce monoclinic structure ($C2/m$, $Z = 2$), also found in Gd and Nd [13] and the α-U-type structure ($Cmcm$, $Z = 2$) reported in Ce, Pr and Nd [14] can also be obtained by a displacive mechanism from the fcc structure. The fcc-α' mechanism, represented in fig. 2(e) consists of antiparallel shift of the atoms pertaining to the $(001)_{\mathrm{fcc}}$ layers along the $\pm[11\bar{2}]$ directions, whereas the α-U structure results from shifts along $\pm[010]$ of the atoms located in (100) layers (fig. 2(f)). Note that the α-U structure coincides with the orthorhombic structure found for non-critical atomic shifts in the Burgers mechanism. The α'-Ce structure corresponds to a Bain-deformed α-U structure.

Table I summarizes the order-parameters symmetries associated with the displacive mechanisms depicted hereabove, in the framework of the Landau theory [1]. In this table the bcc phase is taken as the parent structure for all the lanthanide structures using the connection, shown in fig. 3(a), between the N-point of the bcc Brillouin zone (BZ), and the X and L points of the fcc BZ. One can deduce from table I the remarkable result, illustrated in fig. 3(b), that *all the displacive transformation mechanisms which give rise to the lanthanide structures cor-*

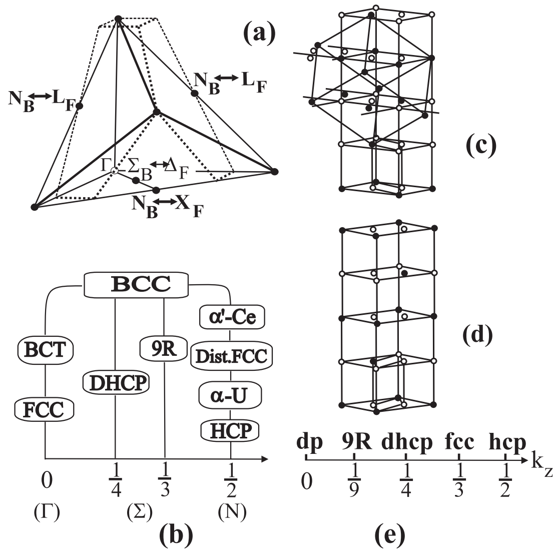

Fig. 3 – (a) Geometrical connection between the N-point of the bcc BZ and the X and L points of the fcc BZ. (b) Connections between the lanthanide structures and the critical wave vectors on the Σ-line. (c) and (d) Ordering mechanisms transforming the disordered polytype (dp) structure into fcc (c) and dhcp (d). (e) Critical wave vectors of the hexagonal BZ associated with the lanthanide phases.

*respond to critical **k**-vectors located on the same* Σ*-line and phonon branch of the bcc BZ.* More precisely, the same six-dimensional irreducible representation (IR) of the $Im\bar{3}m$ space-group at the BZ boundary N-point induces the hcp, α-U, distorted fcc and α′-Ce structures for different equilibrium values of the order-parameter components. A two-dimensional IR at the Γ BZ center yields the fcc and bct structures, whereas twelve-dimensional IRs at two distinct points of the Σ-line lead to the dhcp and 9R structures.

The preceding analysis allows to understand the order in the basic sequence of reconstructive phase transitions found in the lanthanide elements with increasing pressure: hcp → 9R → dhcp → fcc. It corresponds to a *decrease of the critical **k**-vector along the* Σ*-line from the boundary* N*-point to the center* Γ. Once the fcc phase is reached, another typical sequence of displacive (non-reconstructive) transitions takes place (fcc - dist.fcc - α′-Ce - α-U) associated with the same critical ***k***-vector at the N-point of the bcc BZ. However, both phase sequences are found only in Gd and Sm, *i.e.* in the middle of the lanthanide series. In the first five elements of the series (La-to-Pm), the hcp and 9R phases are absent. Conversely, from Tb-to-Tm the fcc and derived structures are absent. This apparent exclusion between the hcp and 9R structures, on the one hand, and the fcc and derived structures, on the other hand, can be explained by considering the ubiquitous role played by the tensile strain ζ_1 in the transformation mechanisms of lanthanides.

As shown in table I (column (d)), ζ_1 coincides with the *primary* order parameter for the bcc-fcc Bain-deformation mechanism. ζ_1 takes a large critical value ($e_{xx} = e_{yy} = \sqrt{3}/2 - 1$, $e_{zz} = \sqrt{3/2} - 1$, $\zeta_1^{\mathrm{fcc}} \simeq 0.29$) corresponding to the drastic change in the angle θ between the diagonals of the $(110)_{\mathrm{bcc}}$ plane: $\theta_{\mathrm{bcc}} = 70^\circ 32$ and $\theta_{\mathrm{fcc}} = 90^\circ$. At the bcc-hcp and bcc-9R transformation, although ζ_1 represents a *secondary* order-parameter (column (f) of table I), it takes the same critical value due to the magnitude of the deformation corresponding to the close packing of atoms in the $(\bar{1}10)_{\mathrm{bcc}}$ plane. In the La-to-Pm group, the fcc phase occupies a central area of the phase diagram, and in the low-pressure range it has a wide region of coexistence with the bcc phase in which specific coherency stresses (corresponding to ζ_1^{fcc}) are involved. These coherency stresses forbid the onset of the strains ζ_1^{hcp} and ζ_1^{9R} giving rise to the hcp and 9R structures, leading ultimately to the formation of a dhcp structure. Reciprocally, in the Tb-to-Tm group the region of coexistence between the bcc, hcp and 9R phases produces coherency stresses discarding the fcc phases. It remains to understand why the hcp, 9R and fcc structures are able to coexist in the phase diagrams of Sm and Gd. Let us show that this property can be related to an interplay between ordering and displacive processes.

The ordering contribution to the transformation mechanisms in lanthanides is revealed by indirect observations. For example, in the La-Pm series the phase diagrams show a narrowing of the hysteretic region separating the fcc and dhcp phases [15] toward low pressures and high temperatures. The limit of stability lines bounding this region merge towards an almost second-order fcc-dhcp transition regime incompatible with the large atomic shifting that would be necessary to transform the fcc structure into dhcp via a purely displacive mechanism. More generally, the occurrence of the dhcp and 9R polytypes, as well as the existence of a high density of stacking faults reported in the hcp and fcc structures [16], denote a clear tendency to the polytypism which underlies the ordering transitions between close-packed structures [1]. In the theoretical description of these transitions [1, 17], one assumes a virtual parent disordered polytype structure formed by a stack of hexagonal monolayers. The hcp, fcc, dhcp and 9R structures result from different ordering processes from the parent disordered structure. Figures 3(c) and (d) illustrate the mechanisms transforming the polytype structure into the fcc and dhcp structures. Figure 3(e) summarizes the results of a Landau analysis, which reveals that the corresponding critical wave vectors leading to the hcp, fcc, dhcp and 9R ordered polytypes are located on the same P-line $[\boldsymbol{k} = (\frac{4\pi}{3}, \frac{4\pi}{3}, k_z)]$ of the hexagonal BZ, the k_z component condensing, respectively, at π/c (hcp), $2\pi/3c$ (fcc), $2\pi/4c$ (dhcp) and $2\pi/9c$ (9R). Such considerations provide an alternative unifying interpretation of the different sequences of transformations in lanthanides, and suggest the following classification of their mechanisms:

1) The dhcp-fcc transformation has an essentially reordering mechanism, as attested by its weakly first-order character and by the total absence of phonon softening on approaching the transition from the dhcp or fcc sides [18]. In the phase diagrams of lanthanides this transformation realizes a crossover between two regimes in which the transitions are predominantly of the displacive type: i) the displacive reconstructive hcp-9R transition which is found in Tb, Dy, Ho, Er and Tm, and ii) the group-subgroup related displacive transitions from the fcc phase to the dist.fcc, α'-Ce, bct, or α-U phases, exhibited by La, Ce, Pr, Nd and Sm.

2) In Sm and Gd, in which the full sequence of displacive and reordering transitions take place, the reordering nature of the dhcp-fcc transition allows stabilization of the fcc structure by reducing the coherency stresses imposed by the hcp and 9R structures. In contrast, in Lu the fcc structure emerges as a distorted phase due to the bcc-dhcp coherency stresses.

3) At low pressure the bcc-hcp transition in Eu and Yb corresponds to a purely displacive mechanism. More experimental data are needed to elucidate the mechanisms giving rise to the high-pressure hexagonal phases (with $Z = 3$ and $Z = 36$) found in these two elements.

At last, let us briefly discuss the connection existing between the crystallogeometrical considerations invoked in our study and the electronic structures of lanthanide elements. The current view in this respect [19–21], is that at ambient and moderated pressures the lanthanide crystal structures are not influenced by the gradual filling of the $4f$-shell, *i.e.* the f-electrons are highly localized and do not participate in bonding. Therefore, the hcp-9R-dhcp-fcc-dist.fcc sequence of phases can be interpreted as for transition metals, in terms of close packing of hard spheres which approximate the electronic shells, whose shape is determined by the mixing of

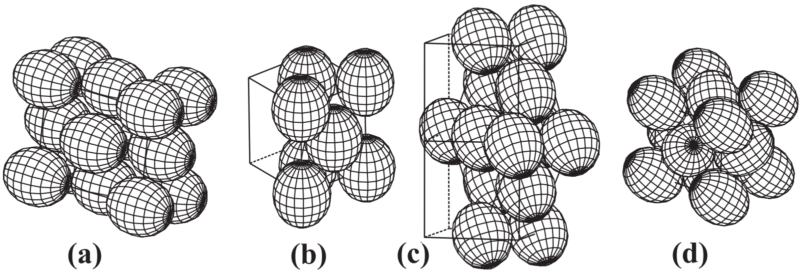

Fig. 4 – Structures of the α-U (a), monoclinic α'-Ce (b), bct (c) and $Pa\overline{3}$ α-Ce (d) phases in terms of packing of ovaloids.

$5d$ and $6s$ electronic levels. A notable exception to the preceding scheme is cerium, in which the volume collapse observed at the isostructural fcc-fcc transition [22] is interpreted by a delocalization of the $4f$-shell. This interpretation in terms of f-electron collapse is also given for explaining the volume changes observed at high pressures in Pr and Gd, when going from the distorted fcc phase to the neighboring (α-U, monoclinic or bct) phases. However in Sm and Nd, the distorted fcc-bct or distorted fcc-monoclinic transitions involve no f-volume collapse [23].

A structural interpretation of the influence of the partial delocalization of the f-electrons at high-pressures, on the crystal structures can be proposed by considering that the itinerant f-electrons participating in the bonding *modify substantially the shape of the electronic shells which behave as non-spherical objects*. Consequently, the close packing of spherical atoms is replaced by the close-packing of less symmetrical atoms, giving rise to the α-U, monoclinic and bct structures. Figures 4(a) to (c) depict the α-U, monoclinic, and bct close-packed structures when assuming an *ovaloid* shape for the electronic shells [24]. Although this concept simplifies the underlying quantum-mechanical considerations, it reflects the property that besides the spherical symmetric part of the lanthanide electron density, described by the spherical harmonics Y_0^0, there exists a quadrupole moment described by the spherical harmonics Y_2^0 which can be constructed from both localized [24] and delocalized [25] f-electron states. The mechanisms leading to these structures consist of different orientational ordering of the ovaloid atoms consistent with the displacive mechanisms. Note that an ovaloid form coincides with the angular dependence of the spherical harmonics Y_2^0, which may approximate the hybridization of the s, p, d and f shells. Thus, the rotation of the ovaloids should occur abruptly in Pr and Gd, or in a continuous way in Sm and Nd. In Ce one can suggest that the γ and α-fcc phase realize two distinct —dynamical and static— disorderings of ovaloid atoms. Thus, the γ form would represent a fcc-packing of effective spheres of rotating ovaloid atoms. The rotations are frozen at the transition to the α-phase that would correspond to a (denser) packing of randomly oriented ovaloids. An alternative description in terms of ovaloid atoms is illustrated by fig. 4(d), which follows the recent suggestion [25,26] that the critical point in Ce is actually a tricritical point. This point would separate a first-order and a second-order transition line between two phases having distinct fcc (γ) and $Pa\overline{3}$ (α) structures.

In summary, we have described comprehensively the symmetry-breaking mechanisms (order-parameters) involved in the structural transitions in lanthanides. These mechanisms provide the basic information for working out the detailed phase diagram of each element, the structure of the phase boundaries, etc. We have also illustrated for the first time for a class of elements the specificity of the mechanisms taking place at reconstructive transitions, showing the typical intercorrelation between displacive and ordering processes which characterize these transitions.

REFERENCES

[1] TOLEDANO P. and DMITRIEV V., *Reconstructive Phase Transitions in Crystals and Quasicrystals* (World Scientific, Singapore) 1996.

[2] GSCHNEIDER K. A. and EYRING L. R. (Editors), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. **17** (North-Holland, Amsterdam) 1993.

[3] YOUNG D. A., *Phase Diagrams of the Elements* (University California Press, Berkeley) 1981 Chapt. 14.

[4] BURGERS W. G., *Physica*, **1** (1934) 561.

[5] BAIN E. G., *Trans. Met. Soc. AIME*, **70** (1924) 25.

[6] DMITRIEV V., GUFAN YU. and TOLEDANO P., *Phys. Rev. B*, **44** (1991) 7248.

[7] WILSON J. A. and DE PODESTA M., *J. Phys. F*, **16** (1986) L121.

[8] BLASCHKO O., DMITRIEV V., KREXNER G. and TOLEDANO P., *Phys. Rev. B*, **59** (1999) 9095.

[9] DMITRIEV V., ROCHAL S., GUFAN YU. and TOLEDANO P., *Phys. Rev. Lett.*, **60** (1988) 1958.

[10] ENDO S., SASAKI H. and MITSUI T., *J. Phys. Soc. Jpn.*, **42** (1977) 882.

[11] HAMAYA N., SAKAMOTO Y., FUJIHISA H., FUJII Y., TAKEMURA K., KIKEGAWA T. and SHIMOMURA O., *J. Phys. Condens. Matter*, **5** (1993) L369.

[12] CHESNUT G. N. and VOHRA Y. K., *Phys. Rev. B*, **62** (2000) 2965.

[13] GROSSHANS W. A. *et al.*, *J. Phys. F*, **13** (1983) L147.

[14] GROSSHANS W. A. and HOLZAPFEL W. B., *Phys. Rev. B*, **45** (1992) 5171.

[15] KRUGER T., MERKAU B., GROSSHANS W. A. and HOLZAPFEL W. B., *High Press. Res.*, **2** (1990) 193.

[16] FREY F. and BOYSEN H., *Acta Crystallogr. A*, **37** (1981) 819.

[17] DMITRIEV V., ROCHAL S., GUFAN YU. and TOLEDANO P., *Phys. Rev. Lett.*, **62** (1989) 2495.

[18] *Landolt-Börnstein. New Series, Group III: Crystal and Solid State Physics*, Vol. **13a** (Springer, Berlin) 1981.

[19] JOHANSSON B. and ROSENGREN A., *Phys. Rev. B*, **11** (1975) 2836.

[20] DUTHIE J. C. and PETTIFOR D. G., *Phys. Rev. Lett.*, **38** (1977) 564.

[21] JOHANSSON B., *J. Alloys Comp.*, **223** (1995) 211.

[22] JOHANSSON B., *Philos. Mag.*, **30** (1974) 469.

[23] ERRANDONEA D., BOEHLER R. and ROSS M., *Phys. Rev. Lett.*, **85** (2000) 3444.

[24] NIKOLAEV A. V. and MICHEL K. H., *Eur. Phys. J. B*, **9** (1999) 619.

[25] NIKOLAEV A. V. and MICHEL K. H., *Eur. Phys. J. B*, **17** (2000) 15.

[26] ELIASHBERG G. and CAPELLMAN H., *JETP Lett.*, **67** (1998) 125.